KAISER•HILL COMPANY

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December 14, 1998

Dear Community Member:

We are sending you six documents which describe results of the fiscal year 1998 (FY98) work, work scope to be initiated in FY99, and the summary from the October 21-22, 1998 Actinide Migration Studies (AMS) Meeting. The enclosed documents are as follows:

- Actinide Migration Studies at the Rocky Flats Environmental Technology Site, Bruce D. Honeyman, PhD., Colorado School of Mines, Golden, Colorado, December 8, 1998;
- Final Report on Phase Speciation of Pu and Am for 'Actinide Migration Studies at the Rocky Flats Environmental Technology Site', Peter H. Santschi, Texas A&M University, Galveston, Texas, October 15, 1998;
- Work Scope Document for 'Actinide Migration Studies at the Rocky Flats Environmental Technology Site' FY99, Bruce D. Honeyman, Colorado School of Mines, and Peter H. Santschi, Texas A&M University at Galveston;
- Actinide Migration at the Rocky Flats Environmental Technology Site, Air Pathway Fiscal Year 1999 Work Plan, Radian International, November 19, 1998;
- Work Plan, Geochemical Support for the Actinide Migration Studies at the Rocky Flats Environmental Technology Site, United States Geological Survey, December 10, 1998; and
- Rocky Flats Environmental Technology Site, Actinide Migration Studies, Meetings: October 21-22, 1998 (meeting summary), December 14, 1998.

In addition, during the October, and November, 1998 stakeholder meetings, the following documents were distributed. If you are interested in obtaining a copy of any of these documents, please contact John Corsi of Kaiser-Hill Company, LLC. at (303) 966-6526. The documents include:

- Loading Analysis for the Actinide Migration Studies at the Rocky Flats Environmental Technology Site, Revision 0, RF/RMRS-98-277.UN, September, 1998;
- Actinide Content and aggregate size Analyses for Surface Soil in the Walnut Creek and Woman Creek Watersheds at the Rocky Flats Environmental Technology Site, RF/RMRS-98-281.UN, Revision 1, September, 1998;
- Conceptual Model for Actinide Migration Studies at the Rocky Flats Environmental Technology Site, October, 1998; and
- Preliminary Report on Soil Erosion/Surface Water Sediment Transport Modeling for the Actinide Migration Study at the Rocky Flats Environmental Technology Site, RF/RMRS-285.UN, November, 1998.

We welcome your comments. Comments that can be reasonably incorporated into this year's work scope will be. On the other hand, if specific comments are beyond this year's scope, they will be considered into next year's activities. Please feel free to call Russell at (303)966-9692 or Chris at (303)966-9887.

Sincerely,

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FINAL REPORT ON PHASE SPECIATION OF PU AND AM FOR 'ACTINIDE MIGRATION STUDIES AT THE ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE'

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15 October 1998

Significant Findings in FY98:

1) Pu and Am concentrations in filterpassing (^{2} 0.45μm) and filter-retained fractions in Walnut Creek at GS03, sampled in August 26-27, 1998, were very low (^{2}1 fCi/L), similar to concentrations of bomb fallout ^{239,240}Pu in natural aquatic systems all over the northern hemisphere.
2) ^{239,240}Pu/^{241}Am activity ratios in both particles as in the ^{2}0.45 μm filter-passing phases were low (i.e., ~1 or below), significantly lower than those in RFETS soils (~5-7).
3) Most Pu and Am (i.e., ~80-90 %) was associated with particles and colloids.
4) However, Pu activity concentrations in the particle-bound fraction was low (i.e., 0.1-0.3 pCi/g), considerably lower than was found in other creeks at RFETS (i.e., ~ 1pCi/g).
5) Significant fractions of Pu and Am which passed a 0.45μm filter were filtered out by 0.1μm and 100kDa ultrafilters, with, on average, about 50% of Pu passing a 100kDa ultrafilter.

Objectives:

1. **To examine the partitioning of Pu and Am between: 1) particulate, colloidal and ^{2}0.45 μm filter-passing phases.**
2. **To determine the chemical nature of the carrier phase (e.g., Fe, Mn, Al, C, etc.).**
3. **To provide data needed for to meet the DQO of the watershed erosion modeling efforts.**

Justification:

The phase speciation of Pu and Am during surface water exceedances is unknown. It is possible that Pu and Am during periods of elevated activity could have been in the colloidal state (i.e., <0.45 μm), which is not considered to be very bioavailable and where metal species complexed by functional groups of microparticles and macromolecules might have a limited lifetime (Wen et al., 1997a). Therefore, experimental determination of phase speciation of Am and Pu, and chemical characterization of the respective carrier phases, will provide the needed information for modeling surface water fate, transport and speciation of Pu and Am. Cross-flow ultrafiltration, CFUF, provides the means to extend our understanding of Pu and Am size distribution to the size realm of microparticles and macromolecules, and to confirm that the truly dissolved fraction of Pu and Am (<100 kDa), is small relative to other size fractions.

Analytical Methods:

The laboratory and analytical aspects include the following:

1) Cross Flow Ultrafiltration (CFUF) evaluation, and
2) surface water sampling.

CFUF evaluation consisted of ultrafiltering 20L of Galveston tap water containing added ^{240}Pu(IV or VI), and ^{242}Pu(IV) used as a yield tracer after two ultrafiltration systems (see below and appendix III). Surface water sampling was conducted only at the end of August 1998 due to delays in contract awards, and low rainfall during the summer months. The protocols of Guo and Santschi (1996,1997) and Wen *et al.* (1996, 1998) were followed for isolating colloidal and particulate phases of metals such as Pu, Am from surface waters by CFUF and ordinary filtration techniques. Chemical parameters which were measured

included total organic carbon (TOC), dissolved organic carbon (DOC), particulate organic carbon (POC), particulate organic nitrogen (PON), anions (fluoride, chloride, nitrate, phosphate, silicate, ...), pH, Al, Fe and Mn of the water, and % organic carbon, in the particulate phases, according to Benoit *et al.* (1994), Guo and Santschi (1997) and Wen *et al.* (1998). In order to have enough water for actinide analysis, different collection and filtration methods were applied to different volumes of water (see Table IA).

A note on terminology: We denote all fractions with either the upper or lower size or nominal molecular weight cutoff limit, or both. The terms "dissolved", "filtrate" are ambigous, and the terms "retentate" and "permeate" are reserved for fractions which were retained by or had permeated an ultrafilter.

On August 26, 1998 140 liters of water was collected in several 25 liter carboys just above the little pond at GS03. The water was transported to the Colorado School of Mines (CSM) where the aliquots of whole water (two 2-liter bottles), were used for SPM, POC sampling and for total (particulate and ^{2}0.45 μm filter-passing) Pu and Am analyses. The remaining containers were emptied and mixed into a 55 gallon plastic drum. On August 27, 1998, 220 liters of water was collected in two types of carboys right at the GS03 site. The water was then transported to CSM and the two 2-liter whole water bottles were used for the determination of SPM and POC concentrations. Two 10-liter carboys were set aside for the determination of total Pu and Am, and the remaining water was emptied in the 55 gallon plastic drum. For both samples the water in the drum was mixed and pumped through 20 μm and 0.45 μm 10 inch MSI Calyx filter cartridges in series. The ^{2}0.45 μm filtered water was collected in 20 liter plastic containers. Forty liters of filtered water was set aside for ultrafiltration through a 0.1 micron (Amicon hollow fiber polysulfone) and a 100kDa (Amicon spiral wound regenerated cellulose) ultrafilter cartridges in parallel. Permeate (or ultra-filtrate) and retentate (colloids) fractions were collected for Pu and Am analysis. 20 liters of filtered water was also measured for Pu and Am and to serve as a ^{2}0.45μm fraction.

The methods for isotope separation were adapted from EPA Method 908.0 (1980), USDOE (1979), USEPA (1979), and Yamato (1982) as described briefly here. Each sample was acidified with concentrated nitric acid to pH <2 and allowed to sit for at least 16 hours. For each sample concentrated hydrochloric acid was added at 5ml/L and ^{243}Am and ^{242}Pu yield tracers were added. The samples were placed on a stir plate and 0.5 ml of 40 mg/ml Fe (III) carrier was added. The pH was measured and concentrated hydrochloric acid added until pH is <1. The sample was covered and stirred for 30 minutes and the pH measured again.

Once the pH was <1, concentrated ammonium hydroxide was added until turbidity remained constant then an additional 50 mls was added. The sample was again covered and stirred. After 30 minutes, the sample was removed from the stir plate, the stir bar removed and the precipitate was allowed to settle. The supernate was decanted until the precipitate slurry could be transferred to 250 ml centrifuge tubes. The samples were centrifuged for 30 minutes at 3000 rpm. Once the supernate was decanted, the precipitate was dissolved in 3 N HCl , transferred to Nalgene bottles and shipped to Texas A&M University. Once at Texas A&M University, the samples were evaporated and redissolved in concentrated HCl to which 75 mls of 9 N HCl and 2 ml saturated sodium nitrite were added. The samples were then run through a series of three anion exchange columns. The first separated the Am from the Pu fractions. The Pu was then microprecipitated on a filter, mounted on a stainless steel planchet and alpha counted. The Am fraction was carried through a methanolic anion exchange column followed by a TEVA resin column. The Am fraction was microprecipitated, mounted on a stainless steel planchette and alpha counted.

Results and Discussion:

Pu and Am results are shown in Table 1, Figures 1 and 2, and Appendix I, and ancillary parameter results in Tables 2-4 and Appendix II. Particulate, colloidal and ^{2}100kDa activities of both nuclides are extremely low. As a consequence, not all the measured activity concentrations are statistically significant, requiring that only a subset of the results reported in Table 1 will be useful for activity balance and phase speciation assessment (Figures 1 and 2). As is evident from Figure 1, most Pu was found in the particulate fraction, with only about 10% passing a 0.45 μm filter. A significant fraction of this "dissolved", ^{2}0.45 μm, fraction, however, was associated with colloids (Figure 2). The exact percentage in these fractions is not as certain as one might wish, as it critically depends on counting statistics and sample size, i.e., how

representative each sample was. However, it was possible to take the best and largest samples from the second day, and come up with an approximate phase speciation scheme, shown in Figure 2 and Table 5, which includes the error limits. They indicate that even at these low concentrations, about half of the Pu is in different colloidal fractions, and half of Pu is found in the truly dissolved (^{2}100kDa) fraction.

Table 1. Results of ^{239,240}Pu and ^{241}Am analysis of surface water samples.

		^{239,240}Pu		^{241}Am		Pu/Am ratio	
Sample	**Size Fraction**	**pCi/L**	**±1σ**	**pCi/L**	**±1σ**	**pCi/L**	**±1σ**
8/26/96							
RF1	Total	LR	LR	0.0040	0.0009	ND	ND
RF3	>20μm	0.0037	0.0003	0.0051	0.0007	0.73	0.12
RF4	>5μm	0.0067	0.0003	0.0033	0.0001	2.01	0.11
RF5	0.45 – 20μm	0.0030	0.0016	0.0019	0.0020	1.59	1.89
RF6	0.45 – 5μm	0.0003	0.00003	0.0002	0.00002	1.76	0.31
RF2	<0.45μm	0.0009	0.0002	0.0006	0.0002	1.60	.56
RF8	0.1 – 0.45μm	0.0009	0.0002	0.0002	0.0002	5.05	6.24
RF7	<0.1μm	0.0005	0.0001	BD	BD	ND	ND
RF10	100kDa – 0.45μm	0.0003	0.0001	LR	LR	ND	ND
RF9	<100kDa	LR	LR	0.0002	0.0001	ND	ND
8/27/98A							
RF13	Total	0.0035	0.0004	HR	HR	ND	ND
RF15	>20μm	0.0043	0.0004	0.0024	0.0003	1.80	0.30
RF16	>5μm	0.0035	0.0001	0.0016	0.0001	2.17	0.11
RF17	0.45 – 20μm	0.0042	0.0007	0.0010	0.0004	4.38	2.02
RF18	0.45 – 5μm	0.0003	0.00003	LR	LR	ND	ND
RF14	<0.45μm (20L)	0.0004	0.0001	0.0002	0.0001	1.85	1.23
RF23	<0.45μm (5L)	0.0008	0.0004	0.0011	0.0006	0.70	0.51
RF21&22	<0.45μm (40L)	0.0004	0.0001	0.0003	0.0001	1.40	0.72
RF20	0.1 – 0.45μm	0.0003	0.0001	LR	LR	ND	ND
RF19	<0.1μm	0.0003	0.0001	0.0001	0.0001	2.53	3.43
8/27/98B							
RF24	Total	0.0015	0.0005	0.0005	0.0003	3.33	2.70
RF26	>20μm	0.0022	0.0003	0.0013	0.0003	1.74	0.46
RF28	0.1 – 0.45μm	0.0002	0.0001	0.0007	0.0002	0.23	0.15
RF27	<0.1μm	0.0002	0.0001	0.00004	0.0001	4.79	13.57
RF30	100kDa – 0.45μm	0.0001	0.0001	0.0001	0.0001	0.98	0.66
RF29	<100kDa	0.0004	0.0001	0.0006	0.0001	0.56	0.24

*) LR = Recovery too low; HR = Recovery to high; ND = No data; BD = below detection limit

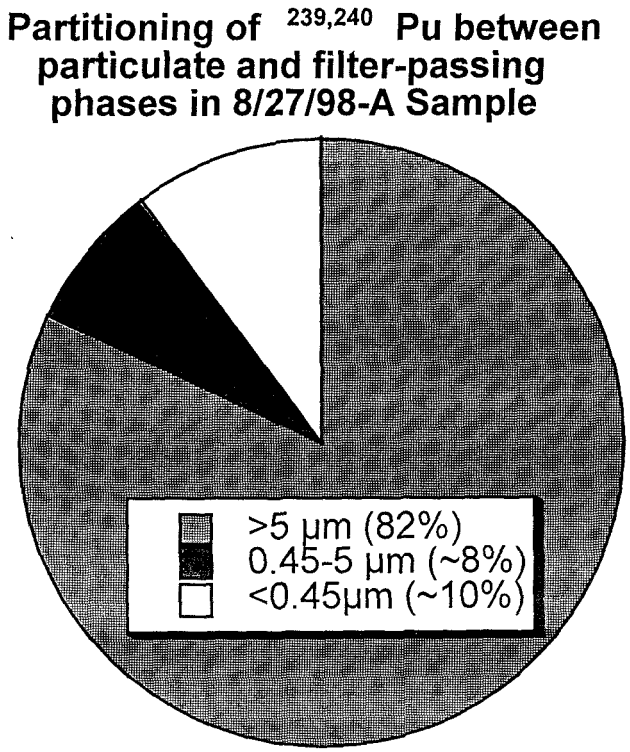

Figure 1. Representative partitioning of ^{239,240}Pu into different size fractions in waters from the Aug. 27 sampling expedition calculated from fractions with significant activities only.

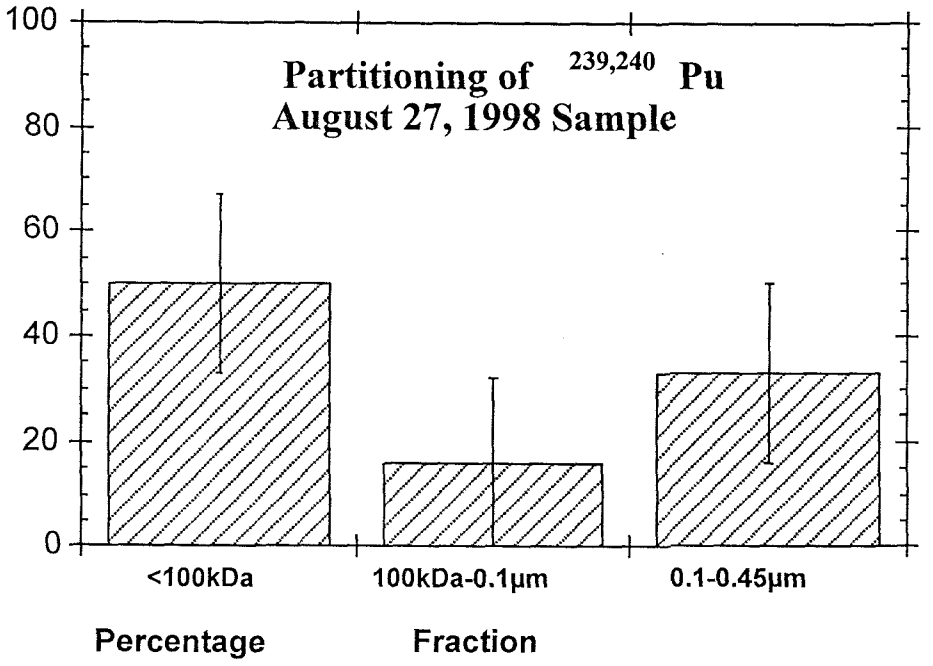

Figure 2. Representative partitioning of ^{239,240}Pu of the < 0.45µm fraction in waters from the Aug. 27 sampling expedition.

It is also noteworthy that these concentrations are 1-2 orders of magnitude below average ^{2}0.45 µm filter-passing Pu concentrations in shallow ground water samples reported by Harnish et al (1994, 1996) and RMRS (1996, 1997). The Pu concentrations we report here are of the same magnitude as those measured from bomb fallout in the 1970's and 1980's in different aquatic environments (Table 6). Furthermore, in our samples, Pu/Am ratios are consistently lower than the average soil ratio of 5-7. Low Pu/Am activity ratios for colloidal and ultrafilter-passing concentrations have also been reported by Harnish et al. (1993, 1996). In many cases, the Pu/Am ratios are not statistically significant, however, due to the fact that many values are close to the detection limit of the method as defined as three times the standard deviation at low values (i.e., ~ 0.0003 pCi/L for both actinides in ^{2}100 L of water). Low activity concentrations coincided with relatively high concentrations of algae and organic carbon in these waters, as is evident from the high organic carbon content of these suspended particles of 18% on 8/26/98 and 30% on 8/27/98. These high biomass and relatively low suspended particulate matter (SPM) concentrations (Table 2) were likely the result of the relatively high nutrient concentrations observed on Aug. 26. The next day, nutrient concentrations were, however, low again (Table 4), but pH remained high (i.e., pH~9.5-9.8, Table 3). Water temperature, Al, Fe and Mn concentrations (Table 3) were significantly lower the second day as well, demonstrating the differences between initial discharge water from just above the small pond (98826) and water sampled 24 hours after discharge began just below the small pond (98827). The August 26 sample was sampled on the first flush from the channel upstream from the small pond at GS03. The August 27 sample was collected on the second day of discharge, below the pond. The pond likely removed the suspended solids and associated constituents (e.g. metals) in the creek flow by settling. Nutrients and organic carbon transformations by aerobic processes might explain the subtle differences in the values measured between the two consecutive days.

Given the actinide concentrations in Table 1, and SPM concentrations given in Table 2, particle-water partition coefficients, Kd, of actinides can be calculated. Pu concentrations in suspended particulate matter

were about 0.1 pCi/g on 8/26, and 0.3 pCi/g on 8/27, while "dissolved" (^{2}0.45 μm) Pu concentrations were 0.008 pCi/L on 8/26, and 0.004 pCi/L on 8/27. Kd values for Pu, calculated as the ratio of particulate Pu to "^{2}0.45 μm filter-passing" Pu were therefore $1.3x10^4$ on 8/26/98, and $7.3x10^4$ (L/Kg, or ml/g)on 8/27/98.

The Pu(IV), Pu(VI) and Am spike recovery experiments with tap water, shown in Figure 3, revealed loss rates of 5-10 %, and a prevalence (~70%) of Pu and Am, regardless of oxidation state, in the ^{2}100 kDa fraction (Figure 3). However, even in tap water, a significant fraction of actinide spike activity was found to be associated with colloids in the 0.1 - 0.45 μm and 100 kDa - 0.1 μm size fractions (Figure 3). While it would have been better to carry out this experiment with Walnut Creek water, it was not possible due to logistical reasons.

Table 2. Summary of data of dissolved organic carbon (DOC), particulate organic carbon (POC) and nitrogen (PON), and suspended particulate matter (SPM) concentrations in water samples collected on August 26-27, 1998.

Sample ID	DOC (mg-C/l)	POC (mg-C/L)	PON (mg-N/L)	POC (mg-C/g)	PON (mg-N/g)	SPM-1 (mg/l)*	SPM-2 (mg/L)*
8-26-98	12.3±0.6	13.1±1.8	1.92±0.24	177±17	26±3	87.7±15	75±18
8-27-98A	14.0±1.0	10.1±0.3	1.37±0.01	304±5	41±1	27.1±5.6	33.2±0.6
8-27-98B	11.9±1.5	9.8±0.5	1.31±0.08	296±11	40±1	34.5±0.3	33.0±3.1

*) Data of SPM-1 and SPM-2 are derived from Nuclepore filters ^{2}0.45 μm and GF/F filters, respectively.

Table 3. Data of trace metal (Fe, Al, and Mn) concentrations (in µg/L) and water temperature (°C), dissolved oxygen, DO (mg/l), and pH in ^{2}0.45 µm water samples collected on August 26-27, 1998.

Sample ID	Fe (µg/L)	Al (µg/L)	Mn (µg/L)	Water Temp (°C)	DO (mg/L)	pH	Alk (meq/l)
8-26-98	43.4±1.4	85.2±3.9	43.3±1.8	25	7.7	9.5	-
8-27-98-A	13.8±1.3	21.7±5.7	22.0±5.8	19.6	8.2	9.8	2
8-27-98-B	12.1±4.1	22.2±5.9	20.9±5.4	19.4	7.9	9.8	2

Table 4. Data of anion (F, Cl, NO_3, HPO_4, Si) concentrations in ^{2}0.45 µm water samples collected on August 26-27, 1998.

Sample ID	F (mg/l)	Cl (mg/L)	NO_3 (mg/L)	HPO_4 (mg/L)	Si (mg/L)
8-26-98	0.42±0.005	91.4±3.2	4.29±0.005	0.79±0.01	5.5±0.05
8-27-98-A	0.34±0.002	92.7±1.2	<0.1	<0.1	5.2±0.07
8-27-98-B	0.33±0.009	93.3±0.4	<0.1	<0.1	4.9±0.01

Table 5: Example of Mass Balance for ^{239,240}Pu sampled on 8/27/98.

		^{239,240}Pu	
		pCi/L	±1σ
	Total (measured)	0.0035	0.0004
Particulate	>5µm	0.0035	0.0001
	0.45 – 5µm	0.0003	0.0000
	>0.45µm (calculated)	0.0038	0.0001
^{2}0.45 µm filter-passing	<0.45µm cartridge	0.0004	0.0001
	Total (calculated)	0.0042	0.0001

Table 6. Comparison of [2]0.45 μm filter-passing concentrations of $^{239,240}Pu$ in different water bodies.

[2]0.45 μm filter-passing Plutonium (fCi/L)	Water Body	Reference
O.4-0.8	[2]0.45 μm, Walnut Creek at GS03	This work
0.3-0.4	[2]0.1μm, Walnut Creek at GS03	"
37	Average total concentration at Walnut Creek at GS03	RF/RMRS-97-131.UN
0.1-0.5	[2]0.45 μm, Great Lakes, 1977	Wahlgren et al., 1980
0.3-1.1	[2]0.45 μm, Narragansett Bay, 1976-1978	Santschi et al., 1980
0.3-1.1	New York Bight, 1976-1977	Santschi et al., 1980
0.1-0.3	[2]0.7 μm, Ob and Yenissey Rivers, 1995	Schwantes, Baskaran and Santschi, 1998, in prep.

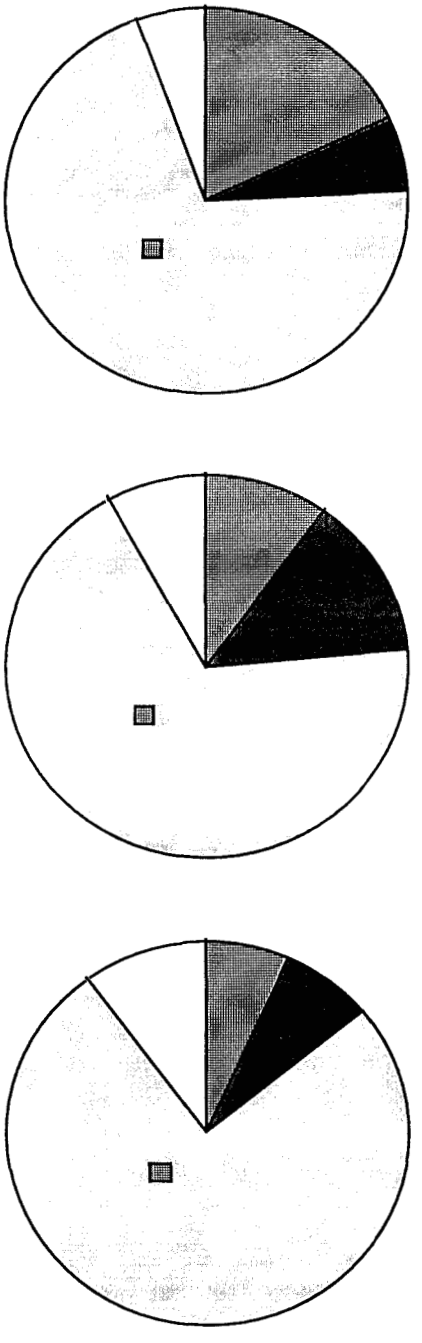

Figure 3. Partitioning of ^{240}Pu and ^{241}Am between different size fractions in tap water passing a 0.45μm filter during spiked laboratory experiments.

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Appendices

Appendix I: Rocky Flats Sample Identification, and Details of Actinide and Ancillary Parameter Results.

Table I-A. Sample Identification

TAMU ID	Sample	Size Fraction	Type	Volume (L)
RF1	98826	Total	Precipitate	4
RF2		<0.45μm	Precipitate	20
RF3		>20μm	Filter paper	10
RF4		>5μm	Cartridge	122
RF5		0.45 – 20μm	Filter paper	
RF6		0.45 – 5μm	Cartridge	122
RF7		<0.1μm	Precipitate	20
RF8		0.1 – 0.45μm	Precipitate	20
RF9		<100kDa	Precipitate	40
RF10		100kDa – 0.45μm	Precipitate	40
RF11		Blank	Precipitate	
RF13	98827A	Total	Precipitate	10
RF14		<0.45μm	Precipitate	20
RF15		>20μm	Filter paper	12
RF16		>5μm	Cartridge	180
RF17		0.45 – 20μm	Filter paper	6
RF18		0.45 – 5μm	Cartridge	180
RF19		<0.1μm	Precipitate	20
RF20		0.1 – 0.45μm	Precipitate	20
RF21+RF22		<0.45μm	Precipitate	40
RF23		<0.45μm	Precipitate	5
RF24	98827B	Total	Precipitate	10
RF25		<0.45μm	Precipitate	20
RF26		>20μm	Filter paper	12
RF27		<0.1μm	Precipitate	20
RF28		0.1 – 0.45μm	Precipitate	20
RF29		<100kDa	Precipitate	40
RF30		100kDa – 0.45μm	Precipitate	40
RF31		Blank	Precipitate	

Table I-B: ^{239,240}Pu and ^{241}Am activities in different size fractions

^{239,240}Pu														
PARTICULATE														
Sample	whole water		> 20 micron		0.45-20 micron		>0.45 (filters)*		> 5 micron		0.45-5micron		>0.45 micron(cartridge)*	
	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-
98826	-	-	0.0037	0.0003	0.0030	0.0016	0.0067	0.0016	0.0067	0.0003	0.0003	0.00003	0.0070	0.0003
98827A	0.0035	0.0004	0.0043	0.0004	0.0042	0.0007	0.0085	0.0009	0.0035	0.0001	0.0003	0.00003	0.0038	0.0001
98827B	0.0015	0.0005	0.0022	0.0003	-	-	-	-	-	-	-	-	-	-
0.45 µm FRACTION														
Sample	< 0.45 micron		0.1- 0.45 micron*		< 0.45 micron* - 100kDa		0.1 - 0.45 micron		< 0.1 micron		100kDa - 0.45 micron		< 100kDa	
	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-
98826	0.0009	0.0002	0.0014	0.0002	-	-	0.0009	0.0002	0.0005	0.0001	-	-	-	-
98827A	0.0004	0.0001	0.0006	0.0001	0.0004	0.0001	0.0003	0.0001	0.0003	0.0001	-	-	-	-
98827B	-	-	0.0004	0.0001	0.0005	0.0001	0.0001	0.000	0.0001	0.0001	0.0001	0.0001	0.0004	0.0001
^{241}Am														
PARTICULATE														
Sample	whole water		> 20 micron		0.45-20 micron		>0.45 (filters)*		> 5 micron		0.45-5micron		>0.45 micron(cartridge)*	
	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-
98826	0.0040	0.0009	0.0051	0.0007	0.0019	0.0020	0.0070	0.0021	0.0033	0.0001	0.0002	0.00002	0.0035	0.0001
98827A	-	-	0.0024	0.0003	0.0010^{m}	0.0004^{m}	0.0034	0.0005	0.0016	0.0001	-	-	-	-
98827B	0.0005	0.0003	0.0013	0.0003	-	-	-	-	-	-	-	-	-	-
0.45 µm FRACTION														
Sample	< 0.45 micron		0.1- 0.45 micron*		< 0.45 micron* - 100kDa		0.1 - 0.45 micron		< 0.1 micron		100kDa - 0.45 micron		< 100kDa	
	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-	pCi/L	+/-
98826	0.0006	0.0002	-	-	-	-	0.0002	0.0002	-	-	-	-	0.0002	0.0001
98827A	0.0002	0.0001	-	-	0.0003^{m}	0.0001^{m}	-	-	0.0001	0.0001	-	-	-	-
98827B	-	-	0.0007	0.0002	0.0007	0.0001	0.0007	0.0002	0.00004	0.0001	0.0001	0.0001	0.0006	0.0001
* = calculated by addition														
- = no data														
^{m} = measured value														
BD = below detection limit														

Table I-C: ^{239,240}Pu and ^{241}Am counting data (+/- signifies ±1σ)

			volume		Detector	Detector Background (cpm)			
Sample	Size Fraction	ID	(L)	Detector	Efficiency	^{242}Pu	+/-	^{240}Pu	+/-
98826	whole water	RF1Pu	4	1	0.20	0.0025	0.0025	0.0003	0.0002
	<0.45 µm	RF2Pu	20	10	0.24	0.0010	0.0010	0.0007	0.0003
	>20 µm	RF3Pu2	10	7	0.20	0.0012	0.0012	0.0003	0.0002
	>5 µm	RF4Pu	122	2	0.20	0.0017	0.0017	0.0002	0.0002
	0.45 – 20 µm	RF5Pu	1	2	0.20	0.0017	0.0017	0.0002	0.0002
	0.45 - 5 µm	RF6Pu	122	3	0.20	0.0010	0.0010	0.0008	0.0004
	<0.1 µm	RF7Pu	20	11	0.22	0.0015	0.0015	0.0005	0.0003
	0.1 - 0.45 µm	RF8Pu	20	8	0.23	0.0008	0.0008	0.0003	0.0002
	<100kDa	RF9Pu	40	12	0.24	0.0006	0.0006	0.0006	0.0003
	100kDa - 0.45 µm	RF10Pu	40	4	0.19	0.0007	0.0007	0.0002	0.0002
	Blank spike	RF11Pu	1	4	0.19	0.0013	0.0013	0.0003	0.0002
98827A	whole water	RF13Pu	10	5	0.25	0.0002	0.0002	0.0002	0.0002
	<0.45 µm	RF14Pu	20	5	0.25	0.0002	0.0002	0.0002	0.0002
	>20 µm	RF15Pu	12	6	0.19	0.0005	0.0005	0.0008	0.0004
	>5 µm	RF16Pu	180	11	0.22	0.0015	0.0015	0.0005	0.0003
	0.45 – 20 µm	RF17Pu	6	7	0.20	0.0010	0.0010	0.0007	0.0003
	0.45 - 5 µm	RF18Pu	180	8	0.23	0.0015	0.0015	0.0005	0.0003
	<0.1 µm n	RF19Pu	20	6	0.19	0.0007	0.0007	0.0013	0.0005
	0.1 - 0.45 µm	RF20Pu	20	5	0.25	0.0002	0.0002	0.0002	0.0002
	<100kDa	RF21Pu	40	6	0.19	0.0008	0.0008	0.0013	0.0005
	100kDa - 0.45 µm	RF22Pu	40	7	0.20	0.0013	0.0013	0.0003	0.0002
	<0.45 µm	RF23Pu	5	8	0.23	0.0000	0.0000	0.0002	0.0002
98827B	whole water	RF24Pu	10	9	0.23	0.0005	0.0005	0.0008	0.0004
	>20 µm	RF26Pu	12	9	0.23	0.0006	0.0006	0.0006	0.0003
	<0.1µm	RF27Pu	20	9	0.23	0.0005	0.0005	0.0008	0.0004
	0.1 - 0.45 µm	RF28Pu	20	10	0.24	0.0010	0.0010	0.0007	0.0003
	<100kDa	RF29Pu	40	11	0.22	0.0015	0.0015	0.0005	0.0003
	100kDa - 0.45 µm	RF30Pu	40	12	0.24	0.0006	0.0006	0.0006	0.0003
	Blank spike	RF31Pu	1	10	0.24	0.0010	0.0010	0.0007	0.0003

Table I-C cont.

			count time	^{242}Pu		Background corrected		^{239,240}Pu		Background corrected		^{242}Pu		^{239,240}Pu	
Sample	Size Fraction	ID	(min)	counts	+/-	counts	+/-	counts	+/-	counts	+/-	cpm	+/-	cpm	+/-
98826	whole water	RF1Pu	6697	77	8.77	60	19.07	121	11	119	11.12	0.0090	0.0028	0.0177	0.0017
	<0.45 µm	RF2Pu	6831	1540	39.22	1533	39.82	49	7	44	7.37	0.2244	0.0058	0.0065	0.0011
	>20 µm	RF3Pu2	16795	2690	51.87	2670	55.53	227	15.07	221	15.59	0.1590	0.0033	0.0132	0.0009
	>5 µm	RF4Pu	6697	1250	35.37	1239	37.13	2250	47.4	2249	47.41	0.1850	0.0055	0.3358	0.0071
	0.45 – 20 µm	RF5Pu	6171	1310	36.19	1300	37.65	14	3.74	13	3.88	0.2106	0.0061	0.0021	0.0006
	0.45 - 5 µm	RF6Pu	6171	1280	35.71	1274	36.25	103	10.15	98	10.41	0.2064	0.0059	0.0158	0.0017
	<0.1 µm	RF7Pu	6831	1253	35.4599	1243	36.94	24	4.8984	21	5.29	0.1819	0.0054	0.0030	0.0008
	0.1 - 0.45 µm	RF8Pu	6697	1200	34.64	1194	35.10	38	6.16	36	6.36	0.1784	0.0052	0.0053	0.0010
	<100kDa	RF9Pu	6831	91	9.5368	87	10.32	12	3.4644	8	3.99	0.0127	0.0015	0.0012	0.0006
	100kDa - 0.45 µm	RF10Pu	6697	2710	52.04	2705	52.24	49	7	48	7.09	0.4040	0.0078	0.0071	0.0011
	Blank spike	RF11Pu	6171	1190	34.45	1182	35.44	2	1.41	0	2.04	0.1915	0.0057	0.0000	0.0003
98827A	whole water	RF13Pu	6699	1250	35.28	1249	35.30	73	8.54	72	8.61	0.1864	0.0053	0.0107	0.0013
	<0.45 µm	RF14Pu	3882	1010	31.72	1009	31.73	14	3.74	13	3.80	0.2600	0.0082	0.0034	0.0010
	>20 µm	RF15Pu	5696	1080	32.79	1077	32.92	129	11.36	124	11.56	0.1891	0.0058	0.0218	0.0020
	>5 µm	RF16Pu	9858	2340	48.37	2325	50.63	3220	56.71	3215	56.78	0.2359	0.0051	0.3261	0.0058
	0.45 – 20 µm	RF17Pu	6163	826	28.74	820	29.41	50	7.07	46	7.37	0.1330	0.0048	0.0074	0.0012
	0.45 - 5 µm	RF18Pu	6163	1320	36.3	1311	37.48	155	12.45	152	12.58	0.2126	0.0061	0.0246	0.0020
	<0.1 µm	RF19Pu	3882	980	31.262	977	31.37	13	3.6062	8	4.05	0.2517	0.0081	0.0020	0.0010
	0.1 - 0.45 µm	RF20Pu	7216	2330	48.22	2329	48.24	26	5.1	25	5.24	0.3227	0.0067	0.0034	0.0007
	<100kDa	RF21Pu	7216	1470	38.33	1464	38.81	42	6.48	32	7.34	0.2029	0.0054	0.0045	0.0010
	100kDa - 0.45 µm	RF22Pu	6699	830	28.81	821	30.19	19	5.0787	4	5.32	0.1226	0.0045	0.0007	0.0008
	<0.45 µm	RF23Pu	6699	1060	32.51	1060	32.51	8	2.83	7	3.05	0.1582	0.0049	0.0010	0.0005
98827B	whole water	RF24Pu	6699	653	25.55	650	25.77	22	4.69	16	5.33	0.0970	0.0038	0.0024	0.0008
	>20 µm	RF26Pu	6165	1320	36.39	1316	36.56	80	8.94	76	9.12	0.2135	0.0059	0.0124	0.0015
	<0.1 µm	RF27Pu	16777	3950	62.87	3942	63.44	42	6.48	28	9.05	0.2349	0.0038	0.0017	0.0005
	0.1 - 0.45 µm	RF28Pu	6699	1700	41.28	1693	41.83	14	3.74	9	4.37	0.2528	0.0062	0.0014	0.0007
	<100kDa	RF29Pu	6699	566	23.79	556	25.87	16	4	13	4.45	0.0830	0.0039	0.0019	0.0007
	100kDa - 0.45 µm	RF30Pu	6699	1610	40.1	1606	40.29	22	4.69	18	5.07	0.2398	0.0060	0.0027	0.0008
	Blank spike	RF31Pu	16779	4870	69.81	4853	71.84	13	3.61	2	6.71	0.2892	0.0043	0.0001	0.0004

Table I-C cont.

			^{242}Pu tracer added		^{239,240}Pu		Blank corrected				^{239,240}Pu			
Sample	Size Fraction	ID	(dpm)	+/-	dpm	+/-	dpm	+/-	pCi	+/-	pCi/l	+/-	% recovery	+/-
98826	whole water	RF1Pu	1.35	0.01	2.6685	0.8830	2.6681	0.8830	1.2128	0.4014	0.3032	0.1003	3.31	1.05
	<0.45 µm	RF2Pu	1.35	0.01	0.0391	0.0066	0.0386	0.0068	0.0176	0.0031	0.0009	0.0002	68.11	1.84
	>20 µm	RF3Pu2	0.996	0.01	0.0826	0.0061	0.0821	0.0063	0.0373	0.0029	0.0037	0.0003	78.00	1.72
	>5 µm	RF4Pu	0.996	0.01	1.8082	0.0663	1.8078	0.0663	0.8217	0.0301	0.0067	0.0002	90.70	2.80
	0.45 – 20 µm	RF5Pu	0.996	0.01	0.0099	0.0030	0.0095	0.0035	0.0043	0.0016	0.0043	0.0016	103.25	3.09
	0.45 - 5 µm	RF6Pu	0.996	0.01	0.0765	0.0084	0.0760	0.0086	0.0345	0.0039	0.0003	0.0000	104.48	3.07
	<0.1 µm	RF7Pu	1.35	0.01	0.0223	0.0058	0.0219	0.0061	0.0099	0.0028	0.0005	0.0001	62.23	1.91
	0.1 - 0.45 µm	RF8Pu	1.35	0.01	0.0404	0.0073	0.0399	0.0075	0.0182	0.0034	0.0009	0.0002	56.80	1.72
	<100kDa	RF9Pu	1.37	0.01	0.1267	0.0645	0.1262	0.0646	0.0574	0.0293	0.0014	0.0007	3.85	0.46
	100kDa - 0.45 µm	RF10Pu	1.35	0.01	0.0239	0.0036	0.0234	0.0040	0.0106	0.0018	0.0003	0.0000	157.73	3.26
	Blank spike	RF11Pu	0.996	0.01	-0.0001	-0.0017	-0.0005	0.0025	-0.0002	0.0011	-0.0002	0.0011	101.32	3.13
98827A	whole water	RF13Pu	1.35	0.01	0.0777	0.0096	0.0772	0.0097	0.0351	0.0044	0.0035	0.0004	54.24	1.58
	<0.45 µm	RF14Pu	1.35	0.01	0.0178	0.0051	0.0174	0.0054	0.0079	0.0025	0.0004	0.0001	75.64	2.44
	>20 µm	RF15Pu	0.996	0.01	0.1148	0.0113	0.1144	0.0114	0.0520	0.0052	0.0043	0.0004	98.37	3.09
	>5 µm	RF16Pu	0.996	0.01	1.3772	0.0386	1.3768	0.0387	0.6258	0.0176	0.0035	0.0001	109.35	2.51
	0.45 – 20 µm	RF17Pu	0.996	0.01	0.0557	0.0092	0.0552	0.0094	0.0251	0.0043	0.0042	0.0007	65.26	2.39
	0.45 - 5 µm	RF18Pu	0.996	0.01	0.1154	0.0101	0.1150	0.0103	0.0523	0.0047	0.0003	0.0000	91.79	2.71
	<0.1 µm	RF19Pu	1.36	0.01	0.0108	0.0057	0.0103	0.0059	0.0047	0.0027	0.0002	0.0001	95.91	3.16
	0.1 - 0.45 µm	RF20Pu	1.35	0.01	0.0144	0.0031	0.0139	0.0036	0.0063	0.0016	0.0003	0.0001	93.89	2.07
	<100kDa	RF21Pu	1.35	0.01	0.0298	0.0068	0.0293	0.0071	0.0133	0.0032	0.0003	0.0001	77.86	2.14
	100kDa - 0.45 µm	RF22Pu	1.35	0.01	0.0072	0.0088	0.0067	0.0090	0.0030	0.0041	0.0001	0.0001	44.36	1.66
	<0.45 µm	RF23Pu	1.34	0.01	0.0087	0.0039	0.0082	0.0043	0.0037	0.0019	0.0007	0.0004	50.77	1.60
98827B	whole water	RF24Pu	1.35	0.01	0.0340	0.0112	0.0335	0.0113	0.0152	0.0051	0.0015	0.0005	30.83	1.24
	>20 mµm	RF26Pu	0.996	0.01	0.0578	0.0071	0.0574	0.0073	0.0261	0.0033	0.0022	0.0003	92.02	2.65
	<0.1 µm	RF27Pu	1.35	0.01	0.0095	0.0031	0.0091	0.0036	0.0041	0.0016	0.0002	0.0001	74.69	1.32
	0.1 - 0.45 µm	RF28Pu	1.34	0.01	0.0075	0.0035	0.0070	0.0039	0.0032	0.0018	0.0002	0.0001	77.28	1.99
	<100kDa	RF29Pu	1.36	0.01	0.0309	0.0110	0.0304	0.0111	0.0138	0.0051	0.0003	0.0001	28.17	1.33
	100kDa - 0.45 µm	RF30Pu	1.34	0.01	0.0151	0.0043	0.0147	0.0046	0.0067	0.0021	0.0002	0.0001	74.03	1.94
	Blank spike	RF31Pu	1.34	0.01	0.0005	0.0019	0.0000	0.0026	0.0000	0.0012	0.0000	0.0012	88.43	1.46

Table I-C cont.

			volume		Detector	Detector Background			
Sample	Size Fraction	ID	(L)	Detector	Efficiency	^{243}Am cpm	+/-	^{241}Am cpm	+/-
98826	whole water	RF1Am	4	1	0.20	0.0002	0.0002	0.0005	0.0003
	<0.45 µm	RF2Am	20	1	0.20	0.0003	0.0002	0.0005	0.0003
	>20 µm	RF3Am	10	1	0.20	0.0002	0.0002	0.0005	0.0003
	>5 µm	RF4Am	122	11	0.22	0.0008	0.0004	0.0008	0.0004
	0.45 – 20 µm	RF5Am	1	2	0.20	0.0003	0.0002	0.0008	0.0004
	0.45 - 5 µm	RF6Am	122	3	0.20	0.0019	0.0006	0.0003	0.0002
	<0.1 µm	RF7Am	20	2	0.20	0.0003	0.0002	0.0008	0.0004
	0.1 - 0.45 µm	RF8Am	20	2	0.20	0.0002	0.0002	0.0008	0.0004
	<100kDa	RF9Am	40	3	0.20	0.0013	0.0005	0.0003	0.0002
	100kDa - 0.45 µm	RF10Am	40	3	0.20	0.0008	0.0004	0.0003	0.0002
	Blank spike	RF11Am	1	7	0.20	0.0003	0.0002	0.0003	0.0002
98827A	whole water	RF13Am	10	4	0.19	0.0000	0.0000	0.0003	0.0002
	<0.45 µm	RF14Am	20	5	0.25	0.0002	0.0002	0.0002	0.0002
	>20 µm	RF15Am	12	9	0.23	0.0015	0.0005	0.0007	0.0003
	>5 µm	RF16Am	180	12	0.24	0.0006	0.0003	0.0007	0.0003
	0.45 – 20 µm	RF17Am	6	10	0.24	0.0015	0.0005	0.0002	0.0002
	0.45 - 5 µm	RF18Am	180	4	0.19	0.0000	0.0000	0.0002	0.0002
	<0.1 µm	RF19Am	20	4	0.19	0.0000	0.0000	0.0002	0.0002
	0.1 - 0.45 µm	RF20Am	20	5	0.25	0.0002	0.0002	0.0002	0.0002
	<100kDa	RF21Am	40	10	0.24	0.0015	0.0005	0.0002	0.0002
	100kDa - 0.45 µm	RF22Am	40	9	0.23	0.0015	0.0005	0.0007	0.0003
	<0.45 µm	RF23Am	5	8	0.23	0.0000	0.0000	0.0002	0.0002
98827B	whole water	RF24Am	10	1	0.20	0.0002	0.0002	0.0005	0.0003
	>20 µm	RF26Am	12	12	0.24	0.0007	0.0003	0.0007	0.0003
	<0.1 µm	RF27Am	20	6	0.19	0.0008	0.0004	0.0013	0.0005
	0.1 - 0.45 µm	RF28Am	20	2	0.20	0.0003	0.0002	0.0008	0.0004
	<100kDa	RF29Am	40	3	0.20	0.0012	0.0004	0.0002	0.0002
	100kDa - 0.45 µm	RF30Am	40	6	0.19	0.0007	0.0003	0.0013	0.0005
	Blank spike	RF31Am	1	7	0.20	0.0005	0.0003	0.0003	0.0002

Table I-C cont.

			count time			Background corrected				Background corrected		^{243}Am		^{241}Am	
Sample	Size Fraction	ID	(min)	^{243}Am counts	+/-	^{243}Am counts	+/-	^{241}Am counts	+/-	^{241}Am counts	+/-	cpm	+/-	cpm	+/-
98826	whole water	RF1Am	5866	1330	36.48	1329.01	36.48	60	7.75	57.03	7.75	0.227	0.006	0.010	0.001
	<0.45 µm	RF2Am	6984	1170	34.22	1167.65	34.22	42	6.48	38.47	6.48	0.167	0.005	0.006	0.001
	>20 µm	RF3Am	16821	696	26.38	693.17	26.38	86	9.27	77.50	9.27	0.041	0.002	0.005	0.001
	>5 µm	RF4Am	6924	1600	39.97	1594.16	39.97	1290	35.86	1284.16	35.86	0.230	0.006	0.185	0.005
	0.45 – 20 µm	RF5Am	16822	3620	60.14	3614.33	60.14	69	8.31	54.82	8.31	0.215	0.004	0.003	0.000
	0.45 - 5 µm	RF6Am	16822	3840	61.98	3808.81	61.98	191	13.82	185.33	13.82	0.226	0.004	0.011	0.001
	<0.1 µm	RF7Am	6985	1130	33.66	1127.65	33.66	18	4.24	12.11	4.24	0.161	0.005	0.002	0.001
	0.1 - 0.45 µm	RF8Am	5468	455	21.33	454.08	21.33	13	3.61	8.39	3.61	0.083	0.004	0.002	0.001
	<100kDa	RF9Am	6986	961	31	951.58	31	27	5.2	24.65	5.20	0.136	0.004	0.004	0.001
	100kDa - 0.45 µm	RF10Am	5866	11	3.32	6.06	3.32	2	1.41	0.02	1.41	0.001	0.001	0.000	0.000
	Blank spike	RF11Am	7216	7	2.65	4.57	2.65	11	3.32	8.57	3.32	0.001	0.000	0.001	0.000
98827A	whole water	RF13Am	5866	1650	40.56	1650.00	40.56	59	7.68	57.02	7.68	0.281	0.007	0.010	0.001
	<0.45 µm	RF14Am	6846	1560	39.5	1558.85	39.5	32	5.66	30.85	5.66	0.228	0.006	0.005	0.001
	>20 µm	RF15Am	7219	1730	41.61	1719.05	41.61	120	10.95	115.13	10.95	0.238	0.006	0.016	0.002
	>5 µm	RF16Am	6925	1610	40.06	1605.99	40.06	924	30.4	918.99	30.40	0.232	0.006	0.133	0.004
	0.45 – 20 µm	RF17Am	7219	1870	43.22	1859.05	43.22	43	6.56	41.78	6.56	0.258	0.006	0.006	0.001
	0.45 - 5 µm	RF18Am	16823	276	16.61	276.00	16.61	240	15.49	237.16	15.49	0.016	0.001	0.014	0.001
	<0.1 µm	RF19Am	6987	821	28.65	821.00	28.65	14	3.74	12.82	3.74	0.118	0.004	0.002	0.001
	0.1 - 0.45 µm	RF20Am	16793	143	11.96	140.17	11.96	17	4.12	14.17	4.12	0.008	0.001	0.001	0.000
	<100kDa	RF21Am	6912	1510	38.85	1499.52	38.85	28	5.29	26.84	5.29	0.217	0.006	0.004	0.001
	100kDa - 0.45 µm	RF22Am	6884	673	25.94	662.56	25.94	23	4.8	18.36	4.80	0.096	0.004	0.003	0.001
	<0.45 µm	RF23Am	6846	1260	35.5	1260.00	35.5	29	5.39	27.85	5.39	0.184	0.005	0.004	0.001
98827B	whole water	RF24Am	6842	763	27.62	761.85	27.62	19	4.36	15.54	4.36	0.111	0.004	0.002	0.001
	>20 µm	RF26Am	7219	1310	36.12	1304.78	36.12	58	7.62	52.78	7.62	0.181	0.005	0.007	0.001
	<0.1 µm	RF27Am	6846	1590	39.91	1584.23	39.91	30	5.48	20.77	5.48	0.231	0.006	0.003	0.001
	0.1 - 0.45 µm	RF28Am	6842	652	25.53	649.69	25.53	31	5.57	25.23	5.57	0.095	0.004	0.004	0.001
	<100kDa	RF29Am	6842	786	28.04	777.93	28.04	47	6.86	45.85	6.86	0.114	0.004	0.007	0.001
	100kDa - 0.45 µm	RF30Am	16794	1540	39.29	1528.68	39.29	57	7.55	34.36	7.55	0.091	0.002	0.002	0.000
	Blank spike	RF31Am	6846	1290	35.97	1286.54	35.97	17	4.12	14.69	4.12	0.188	0.005	0.002	0.001

Table I-C cont.

			^{243}Am		^{241}Am		blank corrected (dpm)				^{241}Am			
Sample	Size Fraction	ID	dpm added	+/-	dpm	+/-	^{241}Am	+/-	pCi	+/-	pCi/l	+/-	%recovery	+/-
98826	whole water	RF1Am	1.12	0.009	0.0481	0.0067	0.0353	0.0076	0.0160	0.0034	0.0040	0.0009	100.73	2.77
	<0.45 µm	RF2Am	1.12	0.009	0.0369	0.0063	0.0241	0.0073	0.0110	0.0033	0.0005	0.0002	74.33	2.18
	>20 µm	RF3Am	1.12	0.009	0.1252	0.0157	0.1124	0.0161	0.0511	0.0073	0.0051	0.0007	18.32	0.70
	>5 µm	RF4Am	1.13	0.009	0.9103	0.0342	0.8975	0.0344	0.4079	0.0156	0.0033	0.0001	94.08	2.36
	0.45 – 20 µm	RF5Am	1.12	0.009	0.0170	0.0026	0.0042	0.0044	0.0019	0.0020	0.0019	0.0020	93.68	1.56
	0.45 - 5 µm	RF6Am	1.12	0.009	0.0545	0.0042	0.0417	0.0055	0.0190	0.0025	0.0002	0.0000	101.92	1.66
	<0.1 µm	RF7Am	1.12	0.009	0.0120	0.0042	-0.0008	0.0056	-0.0003	0.0025	0.0000	0.0001	70.40	2.11
	0.1 - 0.45 µm	RF8Am	1.12	0.009	0.0207	0.0090	0.0079	0.0097	0.0036	0.0044	0.0002	0.0002	36.21	1.70
	<100kDa	RF9Am	1.13	0.009	0.0293	0.0062	0.0165	0.0072	0.0075	0.0033	0.0002	0.0001	60.78	1.98
	100kDa - 0.45 µm	RF10Am	1.12	0.009	0.0042	0.2607	-0.0086	0.2607	-0.0039	0.1185	-0.0001	0.0030	0.46	0.25
	Blank spike	RF11Am	1.12	0.009	2.1008	1.4656	2.0880	1.4657	0.9491	0.6662	0.9491	0.6662	0.28	0.16
98827A	whole water	RF13Am	1.12	0.009	0.0387	0.0053	0.0259	0.0064	0.0118	0.0029	0.0012	0.0003	132.38	3.26
	<0.45 µm	RF14Am	1.12	0.009	0.0222	0.0041	0.0094	0.0055	0.0043	0.0025	0.0002	0.0001	79.85	2.03
	>20 µm	RF15Am	1.14	0.009	0.0764	0.0075	0.0636	0.0083	0.0289	0.0038	0.0024	0.0003	89.65	2.18
	>5 µm	RF16Am	1.13	0.009	0.6466	0.0268	0.6338	0.0270	0.2881	0.0123	0.0016	0.0001	84.81	2.12
	0.45 – 20 µm	RF17Am	1.13	0.009	0.0254	0.0040	0.0126	0.0054	0.0057	0.0025	0.0010	0.0004	93.37	2.18
	0.45 - 5 µm	RF18Am	1.13	0.009	0.9710	0.0862	0.9582	0.0863	0.4356	0.0392	0.0024	0.0002	7.65	0.46
	<0.1 µm	RF19Am	1.12	0.009	0.0175	0.0051	0.0047	0.0063	0.0021	0.0029	0.0001	0.0001	55.30	1.93
	0.1 - 0.45 µm	RF20Am	1.12	0.009	0.1132	0.0343	0.1004	0.0345	0.0457	0.0157	0.0023	0.0008	2.93	0.25
	<100kDa	RF21Am	1.13	0.009	0.0202	0.0040	0.0074	0.0054	0.0034	0.0025	0.0001	0.0001	78.66	2.04
	100kDa - 0.45 µm	RF22Am	1.12	0.009	0.0310	0.0082	0.0182	0.0090	0.0083	0.0041	0.0002	0.0001	36.88	1.45
	<0.45 µm	RF23Am	1.11	0.009	0.0245	0.0048	0.0117	0.0060	0.0053	0.0027	0.0011	0.0005	71.28	2.01
98827B	whole water	RF24Am	1.12	0.009	0.0228	0.0065	0.0101	0.0074	0.0046	0.0034	0.0005	0.0003	49.50	1.80
	>20 µm	RF26Am	1.13	0.009	0.0457	0.0067	0.0329	0.0076	0.0150	0.0035	0.0012	0.0003	66.18	1.84
	<0.1µm	RF27Am	1.12	0.009	0.0147	0.0039	0.0019	0.0053	0.0009	0.0024	0.0000	0.0001	107.05	2.70
	0.1 - 0.45 µm	RF28Am	1.11	0.009	0.0431	0.0097	0.0303	0.0103	0.0138	0.0047	0.0007	0.0002	41.78	1.64
	<100kDa	RF29Am	1.13	0.009	0.0666	0.0102	0.0538	0.0109	0.0245	0.0049	0.0006	0.0001	50.73	1.83
	100kDa - 0.45 µm	RF30Am	1.11	0.009	0.0249	0.0055	0.0122	0.0066	0.0055	0.0030	0.0001	0.0001	42.49	1.09
	Blank spike	RF31Am	1.12	0.009	0.0128	0.0036	0.0000	0.0051	0.0000	0.0023	0.0000	0.0023	81.99	2.30

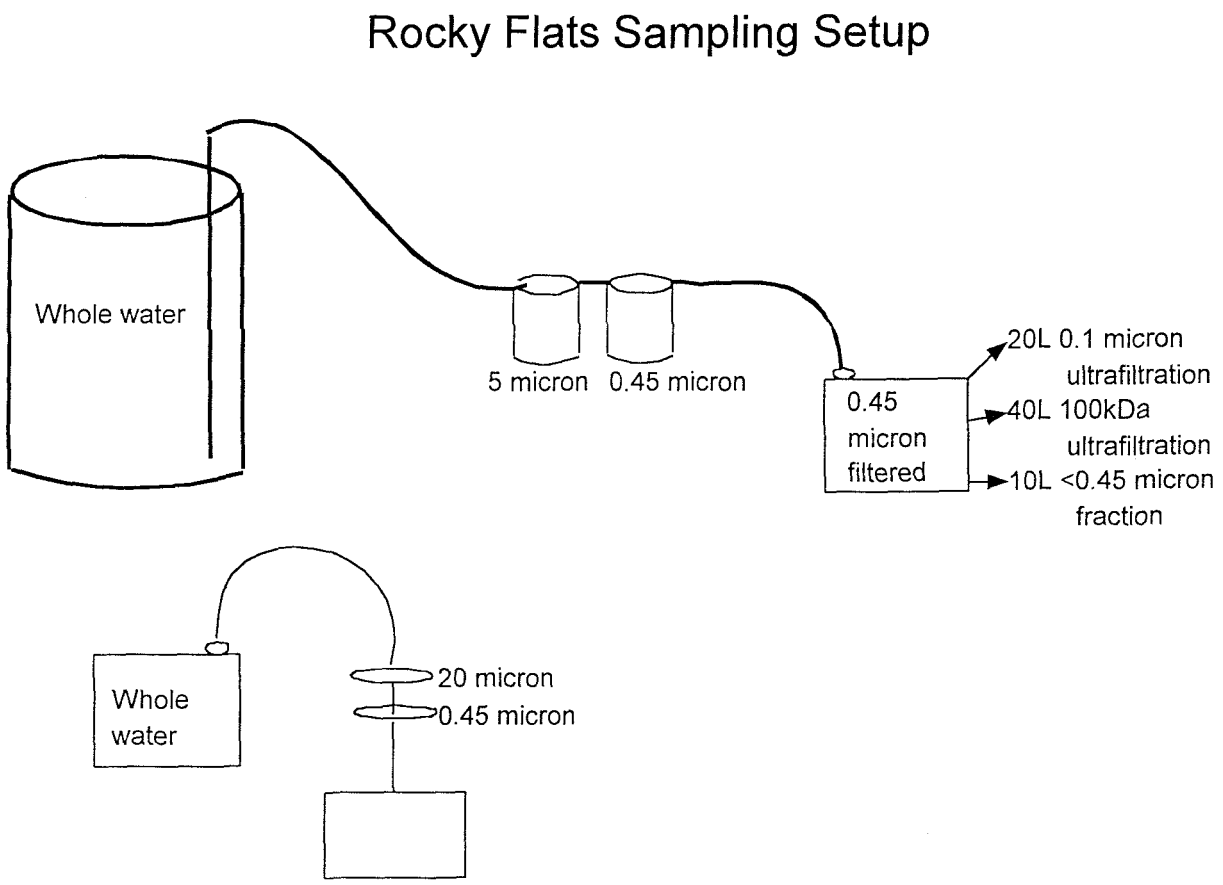

Figure I-A: Rocky Flats Filtration and Ultrafiltration Sampling Setup. Two systems were run in parallel – one for the particulate fractions (>0.45μm and >20μm) , and one for CFUF (cross flow ultrafiltration) experiments.

Appendix II. Detailed Data for SPM, POC, PON, DOC, Fe, Al, Mn, and Anion Concentrations.

August 26-27, 1998 Sampling Trip

Table II-A: Suspended particulate matter (SPM) concentration (³0.45μm):

SS#	Sample ID	Sample	SPM (mg/l)	Avg (mg/l)	±1σ	±1σ (%)
1	98826-1	8/26/98	98.6	87.7	15.4	17.5
2	98826-2*	8/26/98	76.9			
3	98827A-1*	8/27/98-A	23.1	27.1	5.6	20.6
4	98827A-2	8/27/98-A	31.1			
5	98827B-1	8/27/98-B	34.3	34.5	0.3	0.9
6	98827B-2	8/27/98-B	34.7			
	SPM data from GF/F filters					
1	98826-1	8/26/98	87.6	75.0	17.9	23.9
2	98826-2	8/26/98	62.3			
3	98827A-1	8/27/98-A	32.8	33.2	0.6	1.7
4	98827A-2	8/27/98-A	33.6			
5	98827B-1	8/27/98-B	35.2	33.0	3.1	9.3
6	98827B-2	8/27/98-B	30.9			

*: particles lost to the filter holder.

Table II-B: POC/PON (in mg-C/liter):

SS#	Sample ID	Sample	POC (mg/l)	POC (mg/l) Average	±1σ (mg/l	±1σ (%)	PON (mg/l)	PON (mg/l) Avg	±1σ
1	98826-1	8/26/98	14.4	13.1	1.86	14.2	2.09	1.92	0.24
2	98826-2	8/26/98	11.8				1.75		
3	98827A-1	8/27/98-A	9.8	10.1	0.34	3.4	1.37	1.37	0.00
4	98827A-2	8/27/98-A	10.3				1.37		
5	98827B-1	8/27/98-B	10.1	9.8	0.54	5.5	1.37	1.31	0.08
6	98827B-2	8/27/98-B	9.4				1.26		

Table II-C: POC/PON (in mg-C /g particle):

SS#	Sample ID	Sample	POC (mg/g)	POC (mg/g) Average	±1σ (mg/g)	±1σ (%)	PON (mg/g)	PON (mg/g) Average	±1σ (%)
1	98826-1	8/26/98	164.7	177.0	17.4	9.8	23.92	26.01	2.97
2	98826-2	8/26/98	189.2				28.11		
3	98827A-1	8/27/98-A	300.2	303.8	5.1	1.7	41.66	41.16	0.70
4	98827A-2	8/27/98-A	307.4				40.66		
5	98827B-1	8/27/98-B	288.1	296.1	11.3	3.8	38.82	39.76	1.34
6	98827B-2	8/27/98-B	304.1				40.71		

Table II-D: Concentration of dissolved organic carbon (DOC) in ²0.45 µm fraction

SS#	Sample ID	Bottle #	DOC (ppm)	±1σ (ppm)	DOC (ppm) Avg	±1σ (ppm) Avg
1	98826-1	B275	12.43	0.3	12.3	0.6
2	98826-2	B062	12.71	0.2		
3	98826-3	C068	11.62	0.2		
4	98827-1	B153	14.69	0.3	14.0	1.0
5	98827-2	A185	13.22			1.0
98827-1	Trace Metal	13	18			18
98827-2	Trace Metal	15	26			26
98827-1	Nutrient	18	29			26
98827-2	Nutrient	12	26			25
98827-3	Nutrient	10	18			17
98827-4	Nutrient	8	16			16

Table II-F: Concentrations of Anions in ²0.45 µm Fraction:

Sample I.D.	F (mg/L)	Cl (mg/L)	NO_3 (mg/L)	HPO_4 (mg/L)	SO_4 (mg/L)	Si (mg/L)
98827-1	0.33	93.5	<0.1	<0.2	30.7	5.3
98827-2	0.34	91.8	<0.1	<0.2	30.3	5.2
98827-3	0.33	93.0	<0.1	<0.2	30.2	4.9
98827-4	0.34	93.6	<0.1	<0.2	30.9	4.9
98826-1	0.42	87.8	4.3	0.8	32.7	5.5
98826-2	0.41	92.6	4.3	0.8	34.4	5.6
98826-3	0.41	94.0	4.3	0.8	34.7	5.5

Appendix III. Detailed Results from Ultrafiltration Test Experiments

Prior to field sampling, several laboratory tests were completed in the laboratory to determine efficiency of chemical (Tests 1-3) and ultrafiltration (EXP 1-3) procedures (A&B). In all cases deionized or tap water was used and samples were done in duplicate. Approximately 2.7 pCi of tracers ^{240}Pu and ^{242}Pu were added. A brief description of each experiment is as follows:

In Test 1 Pu determination was made using precipitation of $CaPO_4$. ^{240}Pu was added to each sample and the yield tracer ^{242}Pu was added at different stages (before precipitation, before columns, before microprecipitation) of the chemical procedure to determine efficiencies of each step. The percent recoveries were calculated based on the activity of ^{240}Pu measured /activity of ^{240}Pu added. Test 2 was a repeat of test 1 with ^{241}Am also measured. Test 3 was a repeat of test 2 but FeOH was precipitated instead of $CaPO_4$.

For EXP 1 tap water was collected in a large volume container (~100L). The water was filtered to a 0.45μm filter and collected in 20 liter carboys. To each carboy, ^{240}Pu, ^{242}Pu, ^{241}Am and ^{243}Am were added. A 20 liter carboy was used for each ultrafiltration setup 0.1μm, 1kDa, 100kDa. After completion of the ultrafiltration, two washes of the ultrafiltration setups collected processed and counted. The 0.1μm filter was washed with dilute HCl followed by EDTA and the 1kDa and 100kDA filters were washed with dilute HNO3 followed by oxalic acid. EXP 2 was a repeat of EXP 1. EXP 3 was the same as 1 and 2 but Pu (VI) was used instead of Pu (IV).

Table III-A: Percent recovery of 2.7 pCi added during precipitation experiments

	Am-241		Pu-240	
Test 1 ($CaPO_4$)			87.72	+/-2.20
			79.57	+/-1.95
Test 1 ($CaPO_4$)			77.23	+/-1.76
(heated)			66.61	+/-1.22
Test 2 ($CaPO_4$)	82.65	+/-4.47	84.77	+/-2.86
	89.31	+/-3.96	89.50	+/-2.95
Test 2 ($CaPO_4$)	92.65	+/-3.29	82.79	+/-3.15
(heated)	93.39	+/-3.37	75.74	+/-2.88
Test 3 (FeOH)	88.56	+/-3.79	97.79	+/-4.25
	99.21	+/-4.16	96.77	+/-3.16

Table III-B: Mass Balance of ultrafiltration experiments. Values represent % recovery of the 2.7 pCi of analyte (Am-241 or Pu-240) added.

		Am-241							Pu-240					
		0.1μ		1kDa		100kDa			0.1μ		1kDa		100kDa	
		%	±	%	±	%	±		%	±	%	±	%	±
EXP1	Permeate	24.84	1.27	13.68	.67	27.7	1.85		56.96	2.78	35.76	2.25	57.12	2.89
	Retentate	30.66	1.44	35.22	1.77	11.8	0.71		12.81	1.11	30.15	2.13	11.37	1.91
	Wash(%)	-		-		-			-		-		-	
	Sum(%)	55.5	1.92	48.9	1.89	39.5	1.98		69.77	2.99	65.91	3.10	68.49	3.46
EXP2	Permeate (%)	76.33	5.28	31.12	1.45	70.15	4.78		81.85	4.19	28.85	1.87	68.28	3.10
	Retentate(%)	18.08	.98	44.69	1.33	10.44	0.44		10.06	0.68	38.56	2.17	8.27	0.80
	Wash(%)	13.64	3.76	3.9	.36	8.08	1.31		6.83	0.82	1.83	1.54	0.63	0.44
	Sum(%)	108.05	5.37	79.71	1.97	88.67	4.80		98.74	4.32	69.24	3.25	77.18	3.23
EXP3	Permeate (%)								83.58	3.65	77.97	3.04	75.88	3.68
	Retentate(%)								6.54	0.66	10.08	0.80	7.35	0.62
	Wash(%)								-		-		-	
	Sum(%)								90.12	3.71	88.05	3.04	83.23	3.73

Appendix IV. QA/QC

A total of 56 samples were run. The duplicate error ratio (DER) for the 8 samples run in duplicate ranged from 1.5 ± 1.0 to 3.3 ± 1.6. The alpha spectrometers were energy and efficiency calibrated prior to counting of samples. During alpha counting, energy calibration checks were performed once a week. No recalibrations were performed as the peaks remained within 40keV of the expected energy.

The breakdown of tracer recoveries is as follows: two >100%, twenty eight between 75-100%, eighteen <75%, 2<30% and 6<10%. All samples greater than 100% and less than 10% recovery were considered unusable and labeled HR (high recovery) or LR (low recovery). During sample processing one sample was combined with another by mistake, accounting for its high recovery. An explanation for the low recoveries is the difficult matrix, primarily algae, which caused problems with digestion and columns. Matrix spikes were not run as all water collected was processed to a variable degree, and time for processing did not allow it. Laboratory control samples were the basis for the laboratory test samples prior to sampling. Tracer recoveries were 100%. Two blanks were run and all samples were blank and background corrected. The blank values were 0.0058 ± 0.0016 pCi for ^{241}Am and 0.0013 ± 0.0009pCi for ^{239,240} Pu.

ACTINIDE MIGRATION STUDIES AT THE ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE

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Contractor: Kaiser-Hill, LLC
Contract: FY 1998
Date: 8 December 1998

Final Report

Significant results of the FY 1998 study:

1. An electrochemical cell method was developed for regulating experimental system redox potential.
2. $^{239,240}Pu$ solubility (defined as the activity of $^{239,240}Pu$ released from the soil phase upon suspension of soil particles in an aqueous solution) over a range of redox conditions (-90 mV $< E_H <$ +800 mV) is relatively limited. The maximum fractional $^{239,240}Pu$ solubility observed for the experimental conditions was 0.18% of total Pu soil activity. For the conditions of the experiment (10 g L^{-1} soil suspension = 3.1 x 10^3 pCi Pu_T = 2.1 x 10^5 fM), the highest observed 'dissolved' $^{239,240}Pu$ concentration[1] was 3.52 x 10^2 fM.
3. $^{239,240}Pu$ solubility significantly decreases under strongly reducing conditions ($E_H \approx$-90 mV) relative to moderately reducing and oxidizing conditions (+160 $< E_H <$ 800 mV). Dissolved Pu at –90 mV was determined to be 115 fM, for the 10 g L^{-1} soil suspension.
4. The decrease in Pu solubility with a lowering in system E_H suggests that under oxidizing conditions (+160 $< E_H <$ 800 mV), dissolved Pu is in the form of Pu(V) (e.g., PuO_2^+). A decrease in E_H yields a reduction of Pu(V) to Pu(IV).
5. ^{241}Am solubility appears to be independent of system E_H, although FY 99 work will further examine the precision of the Am data at –90 mV. This result is consistent with the redox independence of Am(III).
6. Selective extraction of operationally defined soil phases suggests that $^{239,240}Pu$ and ^{241}Am are chemically separated in the RFETS soil isolates and not 'locked' together in PuO_2(s) particles.
7. Analysis of $^{239,240}Pu$ and ^{241}Am solution-phase activities over a range of reducing conditions suggests that low values in observed $^{239,240}Pu/^{241}Am$ activity ratios may be the consequence of decreased Pu solubility relative to Am, rather than enhanced Am solubility as previously postulated.
8. For the conditions of the experiments, soil constituent solubility (e.g., sesquioxides) was not affected by low E_H values.
9. The selective extraction data indicate that low $^{239,240}Pu/^{241}Am$ ratios in the target 'phases' (e.g., exchangeable) is the consequence of greater relative release of Am compared to Pu.
10. $^{239,240}Pu/^{241}Am$ ratios are similar in a comparison of the sequential extraction 'exchangeable' (1.38 $\pm$ 1.10) and oxidizing (+160 $< E_H <$ 800 mV) suspension (3.44 $\pm$ 1.37) data.

[1] Dissolved or soluble Pu and Am is operationally-defined here as the activity that passes a 0.45μm Nuclepore filter.

1. Introduction.

A wide range of work at Rocky Flats has demonstrated that particulate forms of Pu and Am make up a significant fraction of the actinide inventory in soils and suggests that surface water transport of Pu and Am is dominated by actinide associations with suspended solids. For example, observations that $^{239,240}Pu/^{241}Am$ activity ratios in soils and surface water are relatively 'fixed' at values between 4 and 7 have been invoked to support the hypothesis that Pu and Am have not been physically or chemically separated and share a common environmental fate (i.e., that Pu and Am are 'locked' together in particulate form).

However, many questions remain that can impact approaches to remediation and strategies for long-term site disposition. More specifically, the chemical behavior of actinide-bearing particles in response to changing environmental conditions has not been fully investigated (Higley, 1994). Such chemical behavior includes but is not limited to:

1. The potential for the release of actinides from particles, which may result in release of Pu and Am to the solution phase in ratios not identical to those of the original particles.
2. Potential redox reactions of Pu within and on the surface of particles due to external or internal conditions. This may also affect potential for dissolution and further reactions.
3. The response of 'host' soil-phase constituents, such as Fe, Mn, Si-Al oxides and hydroxides and soil organic matter, to changes in soil redox conditions and the potential of subsequent actinide release from the host phases.

Work during this fiscal year addresses three of questions of relevance to the Site Conceptual Model including:

1. The distribution of Am and Pu between particle and 'solution' phases under oxidizing and strongly reducing soil conditions.
2. The relevance of colloidal forms of Pu and Am in surface water transport.
3. An assessment of the potential for non-particle transport under anoxic soil conditions.

This report describes work that addresses questions 1 and 3. The overall question addressed by FY 98 analytical work is: How general is the assumption of particle transport of Pu and Am?

Figure 1 presents two conceptual models for Pu transport through soils. For many contaminants, transport as a dissolved substance is the primary process by which contaminants are transported through porous media. Figure 1a can be thought of as consisting of two phases: 1) a 'phase' composed of immobile soil constituents and 2) a mobile, aqueous phase. With this scenario, the rate of transport of a contaminant through a soil depends on the velocity of the aqueous phase and the extent to which the contaminant partitions between the immobile soil components and the aqueous phase. Plutonium has a limited solubility and typically is not expected to be transported to any appreciable extent as a soluble species (e.g., Graf, 1994).

Alternatively (Figure 1b), contaminants of low solubility may be transported through porous media through association with a mobile, non-aqueous phase (McCarthy and Wobber, 1993, and references therein). This mobile phase may consist of micro-particles or colloids (1b). With respect to Pu, one possibility is that the mobile materials are composed of micrometer-sized $PuO_2(s)$[2] particles, colloidal mineral species to which Pu is sorbed or organic matter/mineral assemblages. Considerable research has been conducted on the transport of contaminants by

[2] $PuO_2(s)$ is used here as a convention. The exact form of Pu is a matter of discussion.

colloidal materials (e.g., Ryan and Elemelich, 1996) and evidence supports the limited transport of colloid-associated Pu through Rocky Flats soil macropores (e.g., Ryan *et al.*, 1998).

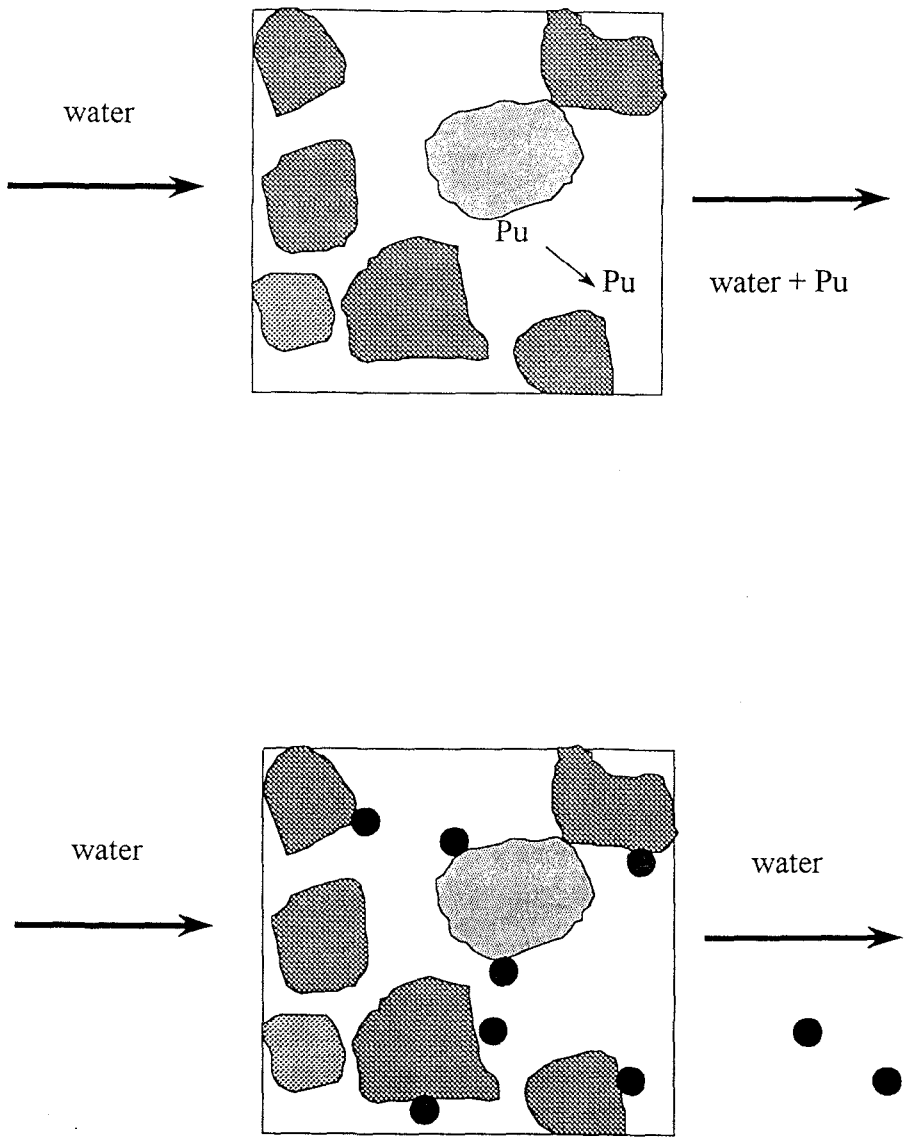

Figure 1. Schematic illustration of two possible scenarios for Pu transport through soils. a) Transport of Pu as a 'soluble' species, including colloidal forms. b) Pu transport as a particle. ● can represent PuO_2(s) microparticles or mineral colloids to which Pu has sorbed.

The work for FY 1998 described herein centers on two aspects of the environmental behavior of Pu at RFETS: 1) the solubility of Pu over a range in soil redox; 2) an examination of hypothesis that Pu in RFETS soils near the 903 Pad may be in the form of $PuO_2(s)$ particles (e.g., McDowell and Whicker, 1978).

2. Materials and Methods.

2.1. Sample locations and form. The soil isolate used for all analyses during the FY's work is sample 97L1879-002. This sample was provided to CSM by Rocky Mountain Remediation Services for the FY 1997 work, from a location SW of the 903 Pad in the 'lip' area. The soil sample consisted of a 'box core' (ca. 10 cm x 10 cm x 10 cm) from which rocks and debris greater than approximately one-half centimeter were removed. Six hundred and forty two grams remained of the original sample. This portion was split using a Humboldt Model H3973 Riffle Splitter by passing the sample through, collecting one-half, passing it through, until eighty grams remained. Thus, three passes were required. The eighty grams were then used as the stock from which individual sample aliquots were taken for analysis.

2.2 Tracers. ^{242}Pu yield tracer. The ^{242}Pu used by CSM was NIST standard solution NIST SRM 4334F at 28.26 Bq g^{-1} with a relative expanded uncertainty (k = 2) of 0.74%. *^{243}Am yield tracer.* The ^{243}Am used by CSM was NIST standard solution NIST SRM 4332D at 36.27 Bq g^{-1} with a relative expanded uncertainty (k=2) of 0.78%.

2.3. ^{239,240}Pu radiochemistry. Aqueous solutions were acidified with nitric acid, ^{242}Pu and ^{241}Am yield tracers were added, and the acidified solutions were taken to dryness on a hotplate. Residues from drying were re-dissolved in nitric acid and treated with sodium nitrite for valence adjustment. Fe carrier was used to co-precipitate the actinides as an iron oxyhydroxide pH adjustment with ammonium hydroxide. The precipitate was removed from solution through centrifugation, re-dissolved with nine molar hydrochloric acid and the solution passed through an anion exchange resin. Pu was then eluted and co-precipitated with neodymium as a fluoride. Finally the microprecipitate was mounted on a filter and assayed using alpha pulse height analysis. Details of the radiochemical separations for Pu can be found in Appendix 2.

2.4. ^{241}Am radiochemistry. The Am fraction was dried on a hotplate then re-dissolved in a nitric acid/methanol solution and further purified using an anion exchange resin to separate the Am from other actinides and matrix elements. The Am was then put through a TEVA Resin™ column using ammonium thiocyanate as a complexing agent to separate the Am from lanthanides and actinium. The Am was then co-precipitated with neodymium as a fluoride. Finally the microprecipitate is mounted on a filter and assayed using alpha pulse height analysis. Details of the radiochemical separations for Am can be found in Appendix 2.

2.5. Selective extraction. A number of selective extraction protocols have been proposed with many tailored to the specific substrates under study. This study followed the general scheme suggested by Yong *et al.* (1993) with a few modifications. The initial soil or sediment mass used in the extraction was 3.0 g.

Exchangeable cations:	8 ml KNO_3 at room temperature; agitation for 1 hour.
Carbonates:	8 ml of 1 M NaOAc adjusted to pH 5 with HOAc; agitation for 1 hour.
Sesquioxides:	20 ml of 0.04 $NH_2OH{\cdot}Cl$ in 25% (v/v) HOAc at 96°C for 6 h.
Organic matter:	Step 1: 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 adjusted to pH 2 with HNO_3 at 85 °C for 2 h; step 2: 3 ml of 30% H_2O_2 at pH 2 and 85 °C for 3 hours with continuous agitation; Step 3: 5 ml of 3.2 M NH_4Oac in 20% (v/v) HNO_3 diluted to 20 ml at room T with agitation for 30 min.
Residual:	Digestion with 5:1 mixture of HF and $HClO_4$; dissolve residue from digestion with 12 M HCl.

2.6 Experimental apparatus for regulating system E_H (or pe).

An environmental isolation system was developed to study the effects of reducing environments on the release of metals and radionuclides from a soil matrix to solution at specified E_H values. The system as utilized:

1. provides a controlled redox environment;
2. allows for the containment a soil/water slurry with constant mixing;
3. allows for periodic spectrophotometric measurements without exposure of samples to oxidizing conditions;
4. provides a variable electrical potential and electron current across the slurry;
5. allows for the relatively rapid determination of system redox potential (E_H);
6. provides the means for rapid separation of the liquid and solid phases, thereby effectively halting further reaction;
7. provides the means to easily monitor and adjust the pH at periodic intervals;
8. allows the removal of samples and the introduce new material and equipment into the isolation chamber without compromising the redox status of the experimental environment.

The following equipment was utilized in the creation of the redox control system (Figure 2):

1. Coy Laboratory Products, Inc. Anaerobic Chamber and associated Manual Airlock (collectively referred to as the glovebox);
2. IBM Instruments, Inc. EC/225 Voltammetric Analyzer (Potentiometer);
3. GeoFilter large diameter filtering apparatus;
4. Orion Model 720 pH meter and electrode;
5. Roy Milton Co. Spectronic 20;
6. 110 volt low RPM stirring motor;
7. An electrochemical cell of in-house design for the regulation of electrochemical potential and sample manipulation (Figure 3).

In addition to the equipment listed above, the following materials were also utilized:

1. A suite of redox indicators (Section 2.7);
2. 0.45 μm large diameter membrane filters;
3. 0.45 μm syringe filters and syringes;
4. a Zeolite O_2 scrubber;
5. O_2 - free nitrogen (<0.5 ppm).

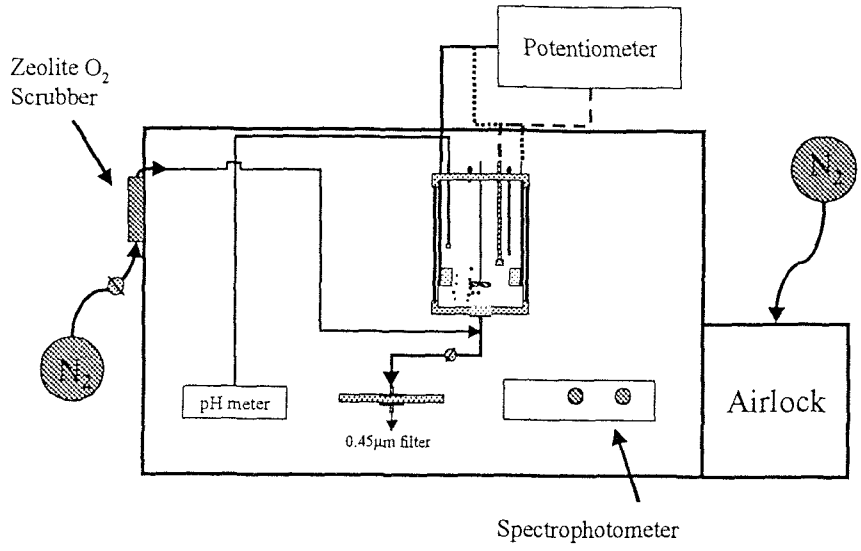

Figure 2. Diagram of the glovebox arrangement developed to maintain reducing conditions. Two sources of N_2 are used to isolate the glovebox interior from ambient O_2: 1) high purity N_2 (<0.5 ppm O_2) is the primary gas for glovebox inflation; 2) high purity N_2 which has been scrubbed of O_2 by a zeolite O_2 trap is used directly for cell sparging. A series of valve manipulations allows *in situ* separation of suspended soil particles from the solution phase through the use of two filters in series: 1) a 5.0 μm stainless-steel prefilter at the cell base (Figure 3); a 0.45 μm Nuclepore filter. Additional equipment includes: an IBM EC/225 Voltammetric Analyzer; an Orion Model 720 pH meter and a Roy Milton Co. Spectronic 20.

2.6.1. *Analysis procedure.* All equipment and materials were introduced into the chamber prior to the evacuation of ambient air and subsequent purging and filling with nitrogen. The equipment internal to the glovebox was disassembled to allow glovebox evacuation to the greatest extent possible. Equipment external to the chamber included the potentiometer, the nitrogen cylinders and the zeolite oxygen trap. Figure 2 is a schematic illustration of the glovebox and associated instrumentation. A pump attached to the airlock was used to purge the glovebox of gas. The chamber was filled with oxygen-free nitrogen and purged for three cycles before the final inflation.

Two sources of nitrogen were used throughout the experimental period. The nitrogen entering through the airlock was not further purified of oxygen from the manufacturer's specification of <0.5 ppm. This N_2 source was used to refill the chamber and airlock after evacuation of ambient air. The second source of <0.5 ppm nitrogen was further scrubbed of O_2 by passing it through a zeolite trap prior to entering the chamber. This second source was fed into the bottom of the cell

through the 5 μm pre-filter/ sparging system that was mounted in the base of the cell apparatus (Figure 3). The filters acted as sparging devices to disperse the nitrogen into the slurry. Throughout the duration of an experiment, a constant flow of nitrogen passed through the cell, over-pressuring the cell and the glove box relative to ambient pressures thereby preventing glovebox gas (< 0.5 ppm O_2) from entering the cell and ambient room air from entering the glovebox. Experience with the cell and glovebox system demonstrated that a tiered gas isolation system is requisite for achieving low E_H values.

A four gram sample was weighed out to the nearest milligram and placed in the cell. Four hundred milliliters of 1.0 mM potassium chloride aqueous solution was also added to the cell. A Teflon-coated impeller attached to a stirring motor kept the slurry well mixed throughout the experimental period. Sufficient redox indicator was then added to the soil/electrolyte slurry such that the initial percent transmittance reading from the spectrophotometer was between 10 and 50 (approximately 1 mM in total indicator). Readings were taken as soon as the indicator was well mixed in order to establish the initial indicator concentration.

Initially, a three electrode system was used to apply a potential to the cell (Figure 3). A silver/silver chloride reference electrode was immersed in the slurry. Two platinum mesh electrodes were sealed in position with their leads protruding upward through the top of the cell. The mesh electrodes were completely immersed in the slurry at diametrically opposed positions near the wall of the cylindrical cell. Eventually, the three electrode system was abandoned in favor of the two electrode system. Since the potential established in the slurry was determined by the indicators, the applied potential had little relevance except in affecting the rate and the stability of the redox process. (It was found that applying a potential of negative two volts over a period of time could have a destructive effect on one or more of the indicators.) Other types of studies may warrant the use of the three electrode system. For the purposes of this study, the two electrode system was found to be simpler and sufficient to provide a stable potential.

2.6.2. *Reduction of NR04.* The following paragraphs describe the procedure followed for the reduction of sample NR04. All samples were reduced using slight variations on the NR04 procedure.

After the NR04/KCl slurry containing the indicator was thoroughly mixed, no potential was applied during the first several hours. Spectrophotometric measurements were taken every few hours to determine if the indicator would be stable in the slurry with no bias applied. A disposable pipette was used to remove several milliliters of slurry from the cell into a clean vessel. A syringe fitted with a 0.45 μm filter was used to remove approximately 4 mL of solution from the settled slurry, leaving as much of the NR04 solids in the vessel as possible.

Since every measurement of this type removed a small amount of solids from the slurry, estimates of the total solids removed were made and corrections for a changing solid/solution ratio were included in data concentration calculations. Solids loss determinations were made by weighing ten dried filters containing filtered solids and comparing to the weight of ten unused filters. In the study of sample NR04, approximately 0.8 grams of solids were removed throughout the 24 day experiment.

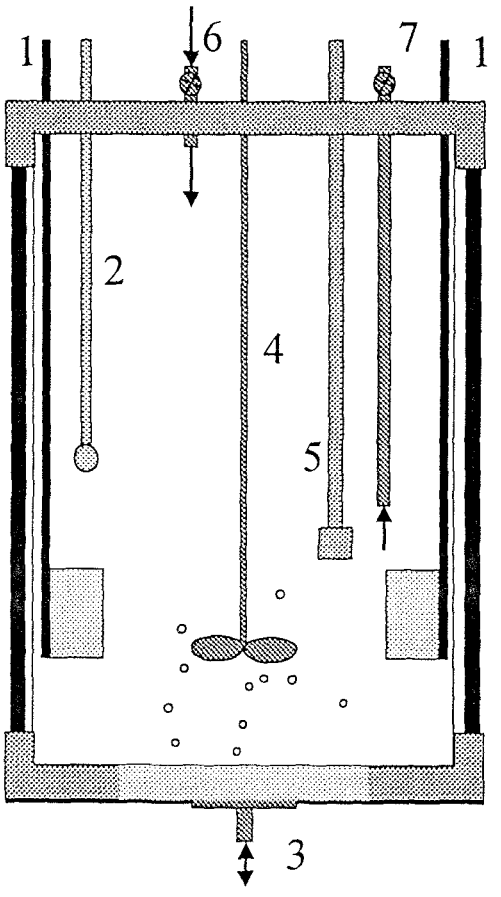

Figure 3. Detail of the cell constructed to regulate system E_H. 1: Platinum electrodes; 2: combination pH electrode; 3: N_2 gas sparger/filtration port with 5.0 μm stainless steel pre-filter and hose bib for connection of the fluid stream to a downstream 0.45 μm Nuclepore filter (Figure 2); 4: Teflon stirrer; 5: reference electrode; 6: N_2 inlet port for cell pressurization; 7: port for slurry extraction.

Indicator analysis (*qq.v.*, Section 2.7). After sample filtration, the separated aqueous phase was immediately put into a photometry cell and measured for percent transmittance at a wavelength of 600 nm. The separated solution was then returned to the cell. Occasionally, the filtered aqueous portion was removed from the glove box to test for reversibility of the reduction reaction. As indicated as part of the indicator selection criteria, indicator reversibility is critical to ensure that loss of the oxidized species color is due to indicator reduction and not loss through processes such as degradation or sorption. Sample oxidation was carried out by bubbling air through the solution for several minutes. On at least two occasions (NR02B and NR03; data not reported), this reversibility was not demonstrated and the experimental data were determined to be invalid.

Sample NR04 showed a fairly immediate drop in color intensity (9.2 to 18.9 % transmittance) prior to applying a potential. Such a reduction may be due to the presence of electron donors in the soil or some other process removing the indicator from solution. Over the course of the

NR04 study, nearly thirty indicator/E_H measurements were made. Of these, five, at intervals throughout the study, were taken to demonstrate reversibility. For all five samples, sparging with ambient air returned the indicator to a percent transmittance value very near the value obtained near the beginning of the study.

The slurry was maintained at a pH of 7.2 throughout the study though step-wise addition of a weak solution of HCl as the solution pH tended to increase as the experiment progressed. Note that the reduction of the oxidized form of the pe indicator (eq. 1) contributes to the consumption of protons and an increase in solution pH.

Sparging the electrochemical cell with N_2 resulted in a small, continuous loss in water. This lost water was periodically replaced when the water level decline was noticeable, that is on the order of 10 milliliters or 2-3% of the total volume. This evaporative loss and water reintroduction introduces a small uncertainty in the measurements..

Once the target E_H and reaction time were obtained, the aqueous phase was quickly separated from the solid phase by pressure filtration: 1) the stirring motor was turned off, the shaft of the propeller disconnected from the motor shaft collar and the propeller shaft allowed to drop below the top of the guide tube through which it spins during operation; 2) the top of the guide tube was sealed off using a connector and plug threaded to match the threads on the connector tube. All other ports were sealed with plugs; 3) the nitrogen sparging line was closed and a connection was made to a second valve at the top of the cell (Figure 3: #6); 4) a third valve was opened at the bottom of the cell allowing the solution to leave the cell and travel through a tube to the filtering device (Figure 3: #3); 5) pressure to the cell was increased to 80 psi and the solution was forced out of the cell through the 5 μm prefilter and 0.45μm Nuclepore filter, and into a receiving vessel; 6) the aqueous solution was then removed from the chamber and the volume measured. In the case of NR04, approximately 66 mL remained in the cell after pressure evacuation. A correction factor (0.835 for NR04) was used in subsequent activity calculations.

After phase separation the aqueous phase was re-oxidized by bubbling ambient air into the solution for a period of several minutes. An aliquot of the solution was then tested in a final check of indicator reversibility. In the case of NR04, the solution was re-oxidized to a final percent transmittance value of 27.9, at 600 nm. The sample was then submitted for $^{239,240}Pu$, ^{241}Am by alpha pulse height analysis and stable elements by inductively coupled plasma analysis.

2.7. Redox indicators. Electrode measurements of soil and sediment E_H values are relatively easy to make but their interpretation is hindered as a consequence of practical and theoretical limitations (e.g., Thorstenson, 1984). More accurate methods of redox determination involve the measurement of *in-situ* oxidized and reduced forms of target indicator elements, e.g., Fe(II)/Fe(III). Problems with this approach include the concentration of indicator elements at or near the detection limit of routine analytical methods and redox-active species that may not be in equilibrium. An additional method of assessing system redox is the addition of colored redox indicators to the system under consideration. Selection criteria for indicators include (after Tratnyek and Wolfe, 1990): 1) the reversibility of the redox couple; 2) that the colors of the indicator must be easily distinguishable in sediment suspensions; 3) that the color of the oxidized

and reduced forms of the indicators must not be strongly affected by pH; 4) that the oxidized and reduced forms of the indicators must have a negligible tendency to sorb; and 5) that the indicators must have a moderate water solubility.

Tratnyak and Wolfe (1990) evaluated a suite of indicators for use in evaluating the redox status of anaerobic sediments. Table 1 lists the properties (Wurmser and Banerjee, 1964) of the redox indicators used in this study.

Table 1. Thermodynamic properties of redox indicators.

Indicator	$E_H^\circ(w)$ (volts)	$pe^\circ(w)$	pe°	log K
2,6-dichloro-indo-phenol	0.217	3.67	10.67	21.3
indigo-5,5',7,7'-tetrasulfonate	-0.046	-0.78	6.22	12.4
Indigo-5,5'-disulfonate	-0.125	-2.11	4.89	9.78

$E_H^\circ(w)$ is the standard electrode potential at pH =7; $pe^\circ = -\log\{e^-\}$ at pH = 0 under standard conditions. In general, E_H and pe are related as follows: $pe = \frac{F}{2.3RT} E_H = 16.9E_H$ in volts at 25 °C. Similarly:

$$pe^\circ(w) = \frac{F}{2.3RT} E_H^\circ(w) = 16.9E_H^\circ(w).$$

$$pe^\circ = pe^\circ(w) + \frac{n_H}{n_e} 7 \text{ and } n_H pe^\circ = \log K.$$

where n_H and n_e are the stoichiometric coefficients (eq. 1) for the transfer of protons (H) and electrons (e).

The redox reactions of all three indicators can be described by the following general reaction:

$$Ox + 2H^+ + 2e^- = Red \quad (1)$$

where Ox and Red represent the oxidized and reduced forms of the indicators, respectively. The concentrations of the oxidized forms were followed through analysis of solution absorbance, relative to a blank, at ~600 nm, the approximate absorbance maxima. The pe corresponding to a calculated loss in the oxidized form was determined from a log α_0 *versus* pe diagram (Figure 4). The fractional reduction of the indicator is defined as

$$\alpha_0 = \frac{[Ox]}{[Ox]+[Red]} \quad (2)$$

The indicators are blue in color when in their oxidized form and are colorless or yellow in their reduced form.

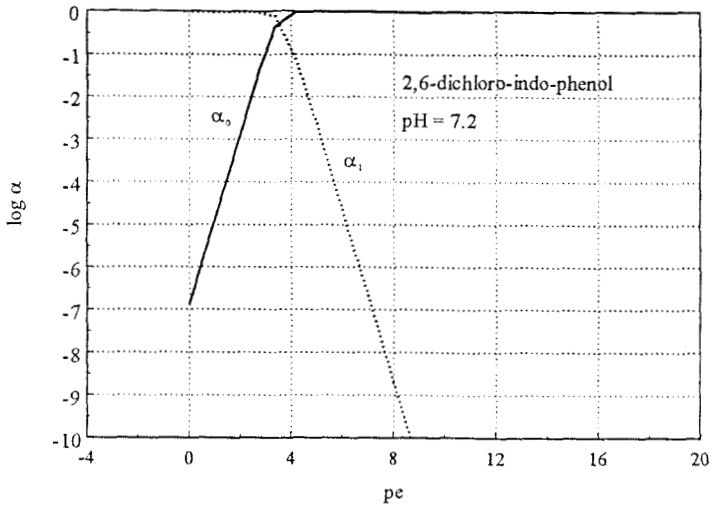

Figure 4. Log fractional distribution (α) of the redox indicator 2,6-dichloro-indo-phenol as a function of pe. See Table 1 for indicator characteristics. α_o is the fraction of the indicator in the oxidized (colored) form; α_1 is the fraction in the reduced form. pe values can be converted to E_H as described in the footnotes to Table 1.

2.8 Metals analysis.

Fractions of the actinide-containing solutions were taken from the digested and/or extracted samples for metals analyses. The fractions were diluted with 1 M nitric acid to approximately 15 mL and then submitted for direct aspiration and quantification by inductively coupled plasma emission spectrometry. Dilution corrections were accomplished via the Excel spreadsheet contained in this report.

All metals analyses under this study were performed by Colorado School of Mines Chemistry Department on a Perkin Elmer Optima 3000 inductively coupled plasma emission spectrometer with a Perkin Elmer AS 91 Auto Sampler. The system software provides two techniques for minimizing spectral interferences: inter-element correction and multi-component spectral fitting. Metals were analyzed per Perkin Elmer specifications using standard protocols.

Quality Assurance measures for these analyses include initial calibration with NIST traceable standards, continuing calibration verification throughout the analytical run time. Scandium is utilized as an internal spike for assessing performance parameters. Data review is performed by qualified ICP operators and the ICP laboratory supervisor prior to final reporting.

Appendix 4 contains the raw ICP/AE metals data.

2.9 *Sample identification.*
The following table (Table 2) is a summary of sample identifications.

Table 2. Summary of sample identification numbers.

RFETS Sample	CSM Sample Aliquot	Sample Description
97L1879-002	A,B,C,D,E	3 gram aliquots of sieved soil used for sequential extraction of Pu
97L1879-002	1-6, 1-7	1 gram aliquots of sieved soil used for total digestion analyses of both Pu and Am isotopes
97L1879-002	3-1,3-2,3-3,3-4,3-5	3 gram aliquots of sieved soil used for total digestion analysis of Pu to determine homogeneity
97L1879-002	F,G,H	3 gram aliquots of sieved soil used for sequential extraction of Am
97L1879-002	NR01, NR02, NR04	4 gram aliquots of sieved soil used for reduction experiments under reducing conditions
97L1879-002	NR04 EL. SM	nitric acid wash of the smaller platinum electrode used in the reduction cell for sample NR04
97L1879-002	NR04 EL. LG	nitric acid wash of the larger platinum electrode used in the reduction cell for sample NR04
97L1879-002	NO02	4 gram aliquot of sieved soil used for control information for the reduction experiments under oxidizing (ambient) conditions

3. Results and Discussion.

3.1 $^{239,240}Pu/^{241}Am$ activity ratios.

While extensive evidence exists pointing to a dominant association of Pu with soil and sediment particles, there is great uncertainty as to whether Pu is primarily in the form of plutonium $PuO_2(s)$ microparticles (e.g., Ryan *et al.*, 1998) or if the Pu has been released from the plutonium $PuO_2(s)$ matrix through environmental diagenesis. A strategy followed this year to address this question was to evaluate $^{239,240}Pu/^{241}Am$ activity ratios.

Not all of the Pu in $PuO_2(s)$ is $^{239,240}Pu$. In addition, Pu disposed of in the 903 Pad area contained ^{241}Pu. ^{241}Pu decays to ^{241}Am, which 'grows-in' at its half-life of 433 years. If all of the Pu and Am remained 'locked' in $PuO_2(s)$ particles, and if the only source of Am and Pu was 903 Pad $PuO_2(s)$, then all $^{239,240}Pu/^{241}Am$ ratios in the environment should have the same value. However, data from the Site for soils and surface waters (e.g., DOE, 1997) shows a range of Pu/Am activity ratios, with most of the ratio values falling within the range of 4 to 7. The variability in activity ratios is suggestive that Pu and Am are not 'locked' together but have become differentiated throughout the environment. Alternatively, or in addition, variability in activity ratios may indicate different sources for Pu and Am.

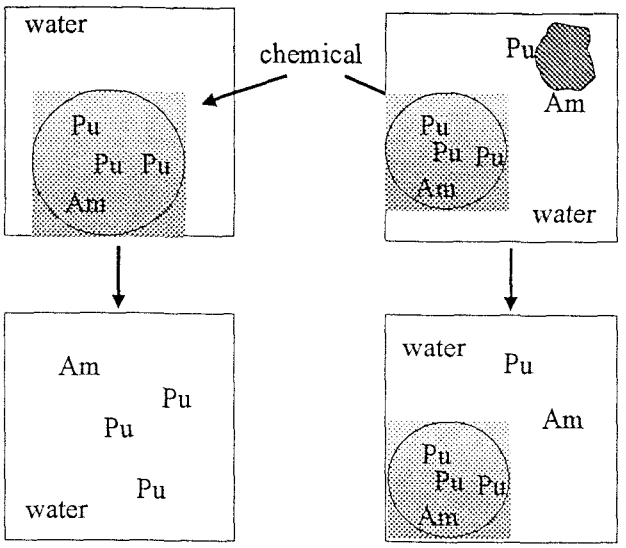

Figure 5. Schematic illustration of the strategy behind the selective chemical attack of soil constituents and evaluation of $^{239,240}Pu/^{241}Am$ ratios.

Figure 5 outlines the strategy followed to evaluate the extent of Pu and Am environmental decoupling. If Pu and Am are 'locked' together in $PuO_2(s)$ particles, the addition of a chemical additive to a soil slurry containing the $PuO_2(s)$, and which is capable of destroying the Pu dioxide, will release the Pu and Am in the activity ratio that they were held in the $PuO_2(s)$ particles. Alternatively, if the Pu and Am are distributed throughout the soil, the addition of chemical agents to a soil slurry that will selectively destroy various soil components should release Pu and Am over a range of activity ratios.

3.1.1 Selective extraction.

A frequently applied method for the analysis of trace element speciation of solid phases is selective leaching (sometimes also called sequential chemical extraction or phase speciation analysis). The methodology is to attack the soil or sediment with increasingly harsh chemical treatments, successively removing the target element from host soil or sediment components. Each of the chemical additions is targeted to destroy a particular class of phases, thereby releasing the 'bound' trace element. A number of different leaching schemes have been proposed over the years; the limitations of such techniques have been thoroughly discussed as well (e.g., von Gunten and Benes, 1995, and references therein). The main limitation of chemical leaching is the low selectivity of the applied chemicals for the target 'phases' (von Gunten and Benes, 1995), i.e.:

1. The extractants often do not quantitatively release the expected form(s), but also attack unwanted forms of the radionuclides;
2. The extractions may significantly change the abundances or properties of the unextracted components in the sample;
3. The extracted radionuclides can re-adsorb on the residue.

The interpretation of selective leaching results may be further complicated when the target metals may undergo redox changes upon application of host-phase extractants. For example, reductants added with the expectation that host mineral phases will reductively dissolve and thereby release the bound target trace metal may also, in some instances, reduce the target metal and alter the metal's association with soil mineral phases. In addition, the effectiveness of selective leaching analysis depends on:

1. Protocol characteristics including the length of time that extractants are in contact with the soil and the order of the various extraction steps;
2. The solid/solution ratio;
3. Soil structure.

It should also be noted that the results of selective leaching analysis provide only a 'snapshot' of the distribution of the target components and, unless supplemented by additional information, do not provide the basis for reaction processes and the future state of the soil or sediment system. However, in spite of the limitations of the approach, selective leaching can be a useful tool for comparing operationally-defined radionuclide speciation as a function of time and space within the same geochemical system.

In spite of the non-specific and operational nature of selective chemical extraction, the technique is valid for evaluating whether RFETS Pu and Am, in the 903 Pad area, are primarily associated with $PuO_2(s)$ particles or dispersed to other soil constituents.

Tables 4 and 5 contain the results of the sequential extraction of $^{239,240}Pu$ and ^{241}Am from soil isolate 97L1879-002. The designation A through E represents the replicate number. Table 7 contains the results of metals analysis for several metals released during each extraction.

The fraction of $^{239,240}Pu$ activity released as the consequence of each extraction step is consistent with the results of FY 1997 work. In summary, the percentage of total activity in each fraction is the following: exchangeable ($1.8 \times 10^{-2} \pm 4.1 \times 10^{-3}$); carbonate ($0.23 \pm 1.9 \times 10^{-2}$); sesquioxide ($3.6 \pm 0.45$); organic ($60 \pm 7.2$) and the residual ($36 \pm 5.5$). In the case of ^{241}Am, the percentage of total activity in each fraction is: exchangeable ($4.3 \times 10^{-2} \pm 2.4 \times 10^{-2}$); carbonate ($1.5 \pm 0.18$); sesquioxide ($9.2 \pm 1.5$); organic ($52.5 \pm 9.8$) and the residual ($37.0 \pm 5.4$).

The following table compares the selective extraction data of Litaor and Imbrahim (1996) with the results of this study. Note that, in addition to the use of different extractants between the studies, this study reversed the organic-carbon/sesquioxide sequence relative to the Litaor and Imbrahim study. Also, Litaor and Imbrahim do not report time/temperature and volume data, precluding a detailed comparison of the two approaches. Litaor and Imbrahim studied soils from several locations to the SE of the 903 Pad as well as samples taken from the soil profiles. This study evaluated one soil isolate and focussed on developing a high degree of replicability.

In spite of these differences in the sample and approach, there is some consistency in the results. In both cases the soluble fraction is low. K^+ (this study) is less effective at exchanging multi-valent ions such as Am(III) than is Ca^{2+}. On the other hand, the magnitude of the exchangeable

fraction in this study is more consistent with the fraction of 'soluble' Pu determined in the redox experiments described below. The organic carbon fractions of both studies are significant as is the residual fraction. Typically, pyrosulfate fusion is more efficient at digesting refractory materials there appears to be little difference between the two studies. The most significant difference is in the magnitude of the sesquioxide fraction and some difference may be the consequence of sequence of steps rather than extractant.

Table 3. Comparison of the results of selective extraction of Pu from RFETS soils: this study and Litaor and Imbrahim.

This study				Litaor and Imbrahim (1996)		
'Phase'	**Procedure**	**% of total**	**[Pu] (fM)**	**'Phase'**	**Procedure**	**% of total**
Exchangeable	KNO_3	0.018 $\pm$ 4.1 x 10^{-3}	7.37 x 10^{2}	Soluble	$CaCl_2$	0.1 – 1.8
Carbonate	NaOAc, pH 5	0.23 $\pm$ 1.9 x 10^{-2}	9.3 x 10^{3}	Carbonate	NaOAc, pH 5	3.3 – 11.1
Sesquioxide	NH_2OHHCl	3.6 $\pm$ 0.45	1.49 x 19^{5}	Organic C	NaOCl, pH 9.2	14.5 – 64.6
Organic C	H_2O_2	60 $\pm$ 7.2	2.5 x 10^{6}	Sesquioxide	CBD*	7.4 – 49.5
Residual	$HF/HCLO_4$ +HCl	36 $\pm$ 5.5	NA	Residual	Pyrosulfate fusion	10.5 – 29.7

*CBD = citrate, bicarbonate and dithionite.

Note that the mass balance (the sum of the fractions *v.* the total digestion) for Am is excellent (Table 5). The mass balance for Pu is poor (Table 4). We believe that the loss of mass balance is due to our inability to completely digest the residual fraction, although mass balances during the FY 1997 work for Pu were much better, using the same technique. We feel that the Pu specific activities from the total digestion are more accurate because of the harsher chemical attack employed in the total analysis (Appendix 1).

3.1.2 Activity ratios from the selective extraction procedure.

The ratio of $^{239,240}Pu$ to ^{241}Am activities for each of the sequential extractions, as well as the bulk ratio, is shown in Figure 6. The activity ratio for the bulk (i.e., 7.08 $\pm$ 2.47) was determined using the average of the total digestions for $^{239,240}Pu$ (310 $\pm$ 55.7: Table 4) and ^{241}Am (43.8 $\pm$ 7.40[3]: Table 5). The exchangeable, carbonate and sesquioxide fractions exhibit $^{239,240}Pu/^{241}Am$ activity ratios that are significantly different from the bulk ratio; the organic and residual fractions are statistically indistinguishable from the bulk. Uncertainties were calculated from the propagation of errors associated with each fraction (e.g., for the exchangeable fraction: $1.38 \pm 1.10 = \frac{0.029 \pm 0.0066}{0.021 \pm .0.012}$). In the case of the three fractions that where the data are statistically distinguishable from the bulk, the smaller $^{239,240}Pu/^{241}Am$ ratio value in the fractions, relative to the bulk, is the consequence of the enrichment of ^{241}Am *in the extractant* relative to $^{239,240}Pu$.

[3] Because only two samples were analyzed for total ^{241}Am, standard deviation could not be determined. Instead the % standard deviation from the sum of fractions (16.9%) was used in the error propagation.

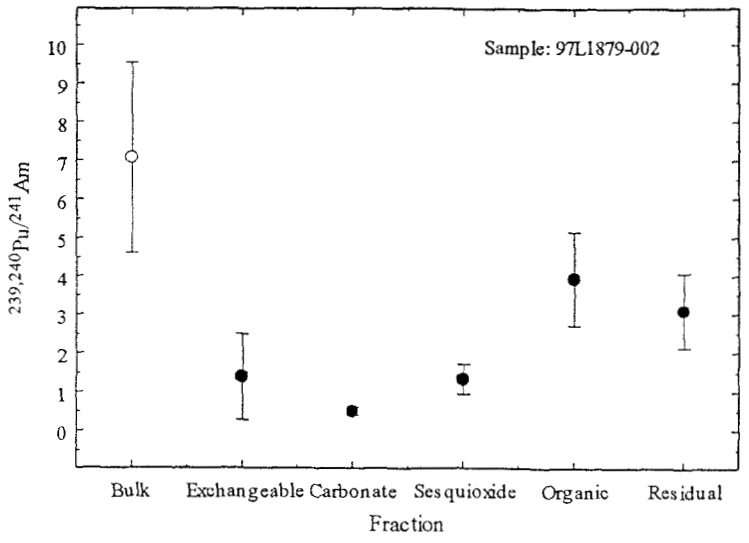

Figure 6. $^{239,240}Pu/^{241}Am$ ratio as a function of extracted soil phase for soil isolate 97L1879-002.

3.2 Analysis of $^{239,240}Pu$ and ^{241}Am solubilities over a range of redox conditions.

The release of $^{239,240}Pu$ and ^{241}Am from fractions of RFETS soil isolate 97L1879-002 suspended in aqueous solution, to solution, was examined as a function of suspension E_H. Details of the experimental system are described in Section 2.6 and 2.7. Summaries of experimental results can be found in Tables 6 and 7; Figure 7 shows $^{239,240}Pu$ and ^{241}Am aqueous-phase activities as a function of slurry E_H. For these experiments, the 'solution' phase was operationally-defined as the portion of the system passing 0.45μm filters. Table 8 contains a summary of the characteristics of each experimental trial.

Table 8. Experimental trial characteristics.

Experiment	Equilibration time (days)	Final E_H (mV)	$^{239,240}Pu$ (pCi L^{-1})	^{241}Am (pCi L^{-1})	Indicator
NO02	1.5	+800	5.17	1.46	none[1]
NR01	1.5	+164	6.17	1.84	2,6-dichloro-indo-phenol
NR02	1.5	-90	1.67	0.287	indigo-5,5',7,7'-tetrasulfonate
NR04	24	-90	1.67	1.32	indigo-5,5',7,7'-tetrasulfonate

[1]NO02 was open to the atmosphere. The E_H was calculated from the stability of H_2O with respect to oxidation at pH 7.2 and $P_{O_2} = 0.17$ atm.

^{241}Am solution phase activities at +800 and +164 mV were, within experimental error, independent of slurry E_H, with an average value of 1.65 pCi L^{-1} (1.98 fM). For the conditions of the experiment (a 10 g L^{-1} soil/water slurry: 438 pCi L^{-1}), approximately 0.38% of the soil ^{241}Am was released to solution. At –90 mV, soil isolates were equilibrated with the aqueous phase for two different time periods: 1.5 and 24 days. The data at 24 d (-90 mV; open square) is statistically indistinguishable from the 1.5 d equilibration data at +800 and + 164 mV; it is not clear at this point whether the data at –90 mV (0.287 pCi L^{-1} and 1.32 pCi L^{-1} for 1.5 and 24 d, respectively) represent statistically-different values. FY 99 work is planed to resolve this issue.

$^{239,240}Pu$ solution-phase activities at +164 and +800 mV are statistically indistinguishable, with an average value of 5.67 pCi L^{-1} (384 fM; n = 2). Using this average value, approximately 0.18% of the soil $^{239,240}Pu$ (10 g L^{-1} = 3.1 x 10^3 pCi L^{-1}) was released to solution upon suspension of the soil isolates in water.

Experimental evaluation of the release of $^{239,240}Pu$ to solution under strongly reducing conditions showed that $^{239,240}Pu$ solution activities exhibited approximately a three-fold decrease as the slurry E_H declined to ca. –90 mV from +164 mV. Note that the data for Pu at –90 mV also represent two equilibration times: 1.5 and 24 days. The data for Pu suggest that changes in the physico-chemical state of Pu occur relatively rapidly under low E_H conditions. Under strongly reducing conditions approximately 0.05% for the soil Pu is solubilized.

Using average values for Pu and Am solution-phase activities, the $^{239,240}Pu/^{241}Am$ activity ratio under oxidizing and moderately reducing conditions (i.e., +800 and +164 mV) is 3.44 ± 1.37. At E_H equal to –90 mV, the ratios are 5.82 and 1.27 for the 1.5 and 24 d equilibration periods, respectively. Again, it is not clear at this point if the difference in the Am values at –90 mV is significant. The data shown in Figure 7 suggest that, under oxidizing and moderately reducing conditions ($+164 < E_H < +800$), Pu and Am are released to solution in a ratio distinct from what is found for the bulk soil (*qq.v.*, Table 5; the bulk ratio is 7.08 ±2.47). However, under reducing conditions, Pu is less soluble relative to oxidizing conditions. If the ^{241}Am data simply reflect the distribution of values about an average, the average ^{241}Am value (n = 4) is 1.23 ±0.66. Under

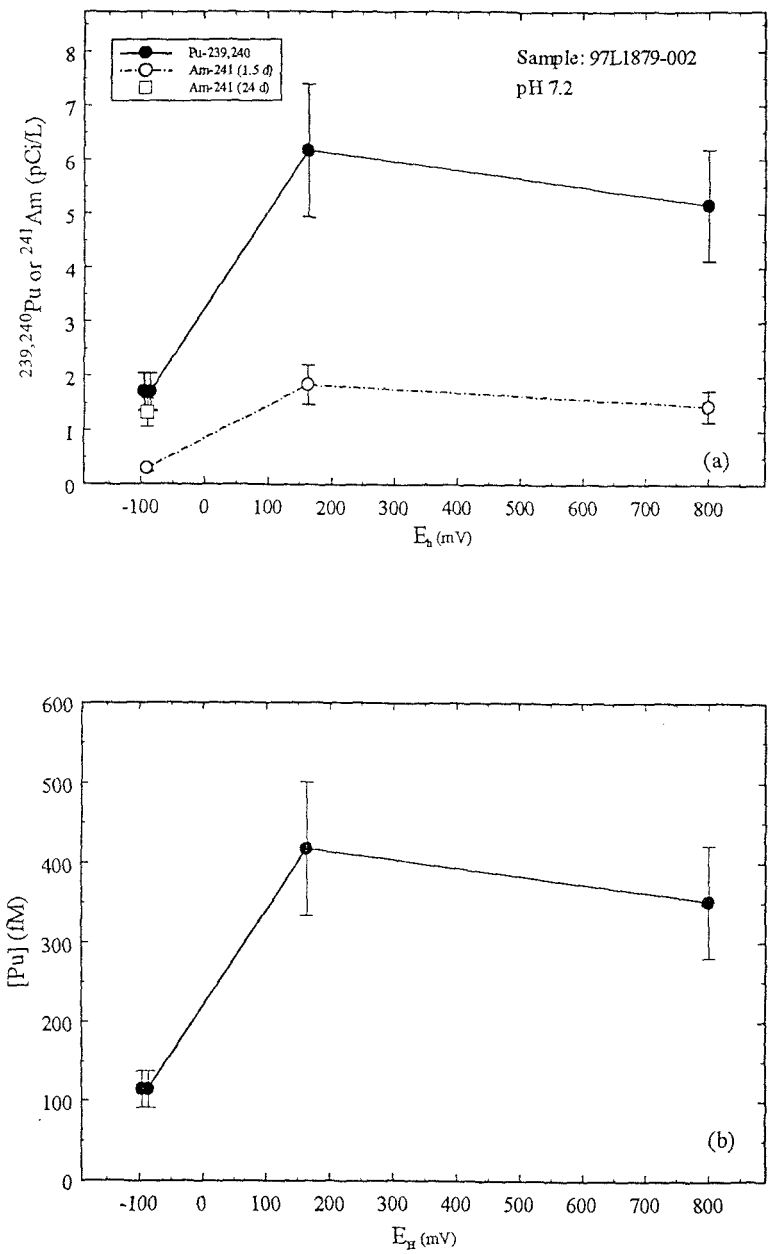

Figure 7. a) ^{239,240}Pu or ^{241}Am activity (pCi L^{-1}) as a function of E_H. The experimental apparatus for the actinide solubility experiments is shown in Figures 2 and 3. In all cases, the soil concentration was 10 g L^{-1} and the initial solution composition was 17 M ohm Nanopure water made 10^{-3} M in KCl. System E_H was determined through the method described in Section 2.7. Table 8 provide details on the individual experiments. The ^{239,240}Pu and ^{241}Am soil activities for the soil isolate are 310 ± 55.7 and 43.8 ± 7.4 pCi g^{-1}, respectively. b) The Pu data presented as concentration (1 fM = 10^{-15} M). Error bars are based on a relative error of 20%.

this assumption, the $^{239,240}Pu/^{241}Am$ release ratio is smaller in value at –90 mV relative to higher E_H conditions. The data suggest that if bulk soil $^{239,240}Pu/^{241}Am$ activity ratios are relatively constant, data for solution-phase $^{239,240}Pu/^{241}Am$ activity ratios may be used as a 'tracer' for soil reducing conditions. Three aspects of the redox experiment data need to be noted. First, the delineation between 'particulate' and 'dissolved' was made operationally: 'dissolved' Pu is defined as the activity of $^{239,240}Pu$ that passed a 0.45 μm Nuclepore filter. Preliminary analysis of the 'dissolved' fraction indicates that ca. 60% of the 0.45 μm filter-passing fraction is colloidal (0.45 μm to 10K Dalton).

Second, only a small fraction of the soil isolate Fe and Mn was solubilized during the reduction experiments. Fe and Mn soil concentrations are, for isolate 971879-02, 18 and 0.37 ppt, respectively. Both concentrations are 2 to 5 times the values reported by Litaor and Imbrahim (1996). For all E_H values, less than 1‰ of the Fe was solubilized in the electrochemical cell indicating that the system, as configured, apparently did not allow for the reductive dissolution of Fe(III) oxides.

Third, both Pu and Am were retained on the Pt electrodes at activity ratios of ca. 4.8 and 5.5 for the small and large Pt electrodes, respectively (Table 6: electrode analysis. Retention of Pu and Am by the electrodes was evaluated at the conclusion of experiment NR04. 'EL. SM' = small Pt. electrode; 'EL LG' = large Pt. electrode). These ratios are statistically indistinguishable from the bulk $^{239,240}Pu/^{241}Am$ ratio of 7.08 ± 2.47. Because Am(III) is not subject to redox transformations, and the electrode mesh has a tendency to foul, it is likely that the electrode buildup is the consequence of the entrapment of fine soil particles that could not be removed by scrubbing.

4. Summary.

1) Under 'normal' RFETS environmental conditions a small fraction of the available plutonium and americium has the potential to be released from the soil into surface and soil waters in soluble form. This report addresses the question, 'How general is the assumption of particle transport of Pu and Am?'. Under 'normal' RFETS soil environmental conditions (oxidizing to mildly reducing) the fractions of soil Pu and Am that are available for release to solution (i.e., not associated with soil particles) are less than 0.18 and 0.38%, respectively. For the conditions of the experiments, the maximum concentration of Pu released to solution was 352 fM (3.52×10^{-13} M); for Am, the average observed concentration over the entire range of E_H values investigated was 1.23 ± 0.66 fM.

   Evidence: The selective chemical extraction (i.e., the 'exchangeable' fraction) and redox (i.e., at an E_H of +800 mV) data sets. Note that soils need to be subjected to strong chemical attack to release greater than 1% of soil Pu into solution.

2) Reducing conditions do not increase the solubility of Pu.

   Evidence: The electrochemical cell data show that under prolonged (24 days) reducing conditions (e.g., -90 mV) Pu 'dissolved' phase concentrations in equilibrium with soil particles

do not increase but, instead, significantly decreased. *Caveat: the experimental system apparently did not provide a condition for the significant reductive dissolution of sesquioxides. This may be the consequence of insufficient reduction potential at the particle surfaces or that abiotic reduction in the system is not efficient.*

3) The 'soluble' Pu fraction is a form of Pu(V).

Evidence: The decrease in Pu solution-phase activities (and concentrations) with decreasing E_H is consistent with the reduction of Pu(V) to Pu(IV) (e.g., Guillaumont and Adloff, 1992). Am(III) activities remain essentially unchanged, as expected from Am electrochemistry, suggesting that the decrease in Pu solubility is due to the formation of relatively insoluble Pu(IV) species.

4) Analysis of ^{239,240}Pu and ^{241}Am solution-phase activities over a range of reducing conditions suggests that low values in observed ^{239,240}Pu/^{241}Am activity ratios may be the consequence of decreased Pu solubility relative to Am, rather than enhanced Am solubility as previously postulated.

Evidence: Data in Figure 7. ^{241}Am(III) activities remain relatively constant (1.23 ± 0.66 pCi L^{-1}) while ^{239,240}Pu activity decreases. *Caveat: it is not clear at this point if the ^{241}Am data at –90 mV, for 1.5 and 24 d, represent real system trends; the data more likely display the degree of precision that can be expected from the complex experimental system.*

5) Selective extraction of operationally defined soil phases suggests that ^{239,240}Pu and ^{241}Am are chemically separated in the RFETS soil isolates and not 'locked' together in PuO_2(s) particles.

Evidence: Data in Figure 5. Evidence suggests that Pu and Am are associated with different soil phases, rather than simply PuO_2(s). If Pu and Am were 'locked' together, one would expect the activity ratios to be statistically indistinguishable throughout the selective extraction sequence.

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Table 4. Replicate sequential extraction data for Pu-239,240.

SAMPLE	FRACTION	MASS OF SAMPLE (G)	TRACER Bq ADDED	TRACER COUNTS	Pu-239/240 COUNTS	COUNT TIME (m)	SAMPLE ACTIVITY (Bq/G)	COUNTING UNCERT. (1σ)(Bq/G)		SAMPLE ACTIVITY (pCi/G)	COUNTING UNCERT. (1σ)(pCi/G)	DETECTOR EFFICIENCY	CHEMICAL YIELD %	PERCENT OF TOTAL ACTIVITY	AVERAGE ACTIVITY (pCi/G)	AVG. OF % TOTAL ACTIVITY	STD DEV ACTIVITY (pCi/G)	PERCEN STD DEV	SAMPLE SPECIFIC MDA (pCi/g)
97L1879-002 A	exchangeable	3.0158	0.158	1170	30	1000	0.00134	0.00025		0.0363	0.0067	0.3152	39.2	0.023					0.016
97L1879-002 B	exchangeable	3.0163	0.152	1726	41	1000	0.00120	0.00019		0.0324	0.0051	0.3152	60.0	0.019					0.010
97L1879-002 C	exchangeable	3.0187	0.152	2616	57	1000	0.00110	0.00015		0.0297	0.0040	0.3152	91.0	0.021					0.0068
97L1879-002 D	exchangeable	3.0127	0.152	2492	48	1000	0.00097	0.00014		0.0263	0.0038	0.3152	86.7	0.015					0.0072
97L1879-002 E	exchangeable	3.0353	0.153	2520	35	1000	0.00070	0.00012		0.0189	0.0032	0.3152	87.1	0.011	0.029	0.018	0.0066	23.0	0.0071
97L1879-002 A	carbonate	3.0158	0.152	2727	832	1000	0.01538	0.00061		0.416	0.016	0.3152	94.9	0.26					0.0065
97L1879-002 B	carbonate	3.0163	0.153	2824	735	1000	0.01320	0.00055		0.357	0.015	0.3152	97.6	0.21					0.0064
97L1879-002 C	carbonate	3.0187	0.152	2792	749	1000	0.01351	0.00056		0.365	0.015	0.3152	97.1	0.26					0.0064
97L1879-002 D	carbonate	3.0127	0.153	2860	773	1000	0.01373	0.00056		0.371	0.015	0.3152	98.8	0.21					0.0063
97L1879-002 E	carbonate	3.0353	0.152	2716	664	1000	0.01224	0.00053		0.331	0.014	0.3152	94.5	0.19	0.368	0.23	0.031	8.4	0.0065
97L1879-002 A	sesquioxide	3.0158	1.22	22218	11429	1000	0.2081	0.0024		5.624	0.065	0.3152	96.3	3.5					0.0065
97L1879-002 B	sesquioxide	3.0163	1.22	22477	14031	1000	0.2525	0.0027		6.824	0.073	0.3152	97.4	4.0					0.0064
97L1879-002 C	sesquioxide	3.0187	1.22	23861	11010	1000	0.1865	0.0021		5.040	0.058	0.3152	103.4	3.6					0.0060
97L1879-002 D	sesquioxide	3.0127	1.22	22510	13520	1000	0.2432	0.0026		6.574	0.072	0.3152	97.6	3.8					0.0064
97L1879-002 E	sesquioxide	3.0353	1.22	23089	11880	1000	0.2068	0.0023		5.589	0.063	0.3152	100.1	3.2	5.930	3.6	0.74	12.5	0.0062
97L1879-002 A	organic	3.0158	5.202	94959	191885	1000	3.486	0.014		94.20	0.37	0.3152	96.5	59					0.0064
97L1879-002 B	organic	3.0163	5.203	94244	221792	1000	4.059	0.016		109.72	0.43	0.3152	95.8	64					0.0065
97L1879-002 C	organic	3.0187	5.207	96433	175321	1000	3.136	0.013		84.76	0.34	0.3152	97.9	60					0.0063
97L1879-002 D	organic	3.0127	5.197	104733	210402	1000	3.465	0.013		93.66	0.35	0.3152	106.6	54					0.0058
97L1879-002 E	organic	3.0353	5.195	99173	242566	1000	4.186	0.016		113.14	0.43	0.3152	100.9	65	99.096	60	12	12.0	0.0061
97L1879-002 A	residual	3.0158	5.182	71636	90330	1000	2.167	0.011		58.56	0.29	0.3152	73.1	37					0.0085
97L1879-002 B	residual	3.0163	5.175	59636	71443	1000	2.055	0.011		55.55	0.31	0.3152	60.9	32					0.010
97L1879-002 C	residual	3.0187	5.154	70749	77808	1000	1.878	0.010		50.75	0.26	0.3152	72.6	36					0.0085
97L1879-002 D	residual	3.0127	5.158	21526	34315	1000	2.729	0.024		73.76	0.64	0.3152	22.1	42					0.028
97L1879-002 E	residual	3.0353	5.148	78446	91919	1000	1.987	0.010		53.71	0.26	0.3152	80.6	31	58.467	36	9.0	15.4	0.0077
Soil Blank 98-01	exchangeable	3.0372	0.148	2501	19	1000	0.000370	0.000085		0.0100	0.0023	0.3152	89.4						0.0069
Soil Blank 98-01	carbonate	3.0372	0.152	2824	7	1000	0.000124	0.000047		0.0034	0.0013	0.3152	98.2						0.0063
Soil Blank 98-01	sesquioxide	3.0372	1.22	22348	17	1000	0.000306	0.000074		0.0083	0.0020	0.3152	96.9						0.0064
Soil Blank 98-01	organic	3.0372	5.228	93682	130	1000	0.00239	0.00021		0.0646	0.0057	0.3152	94.8						0.0065
Soil Blank 98-01	residual	3.0372	5.19	34956	72	1000	0.00352	0.00042		0.095	0.011	0.3152	35.6						0.017
97L1879-02 1-6	Total	1.0102	5.2108	29535	47687	592	8.328	0.062		225.1	1.7	0.3152	50.6		267.9				0.062
97L1879-02 1-7	Total	0.9774	5.1561	38360	83599	592	11.497	0.071		310.7	1.9	0.3152	66.5						0.049
BLK 98-03	Total	0.9997	2.606	15920	174	592	0.028	0.002		0.8	0.1	0.3152	54.6						0.058
97L1879-02 3-1	Total	3.039	1.4834	2742	82200	216	14.63	0.28		395.5	7.7	0.3152	45.2		310.0		55.7	18.0	0.063
97L1879-02 3-2	Total	3.0668	1.4796	3828	73579	216	9.27	0.15		250.6	4.2	0.3152	63.3						0.045
97L1879-02 3-3	Total	3.3182	1.4792	4302	102768	216	10.65	0.17		287.8	4.5	0.3152	71.2						0.037
97L1879-02 3-4	Total	3.3091	1.4717	4098	112915	216	12.254	0.19		331.2	5.3	0.3152	68.2						0.038
97L1879-02 3-5	Total	3.0223	1.5097	17205	362992	1000	10.539	0.082		284.8	2.2	0.3152	60.3						0.010
BLK	Total	3	0.3036	4290	92	1000	0.00217	0.00023		0.0587	0.0062	0.3152	74.7						0.0084

	Sum of Activity from fxns (pCi/G)	Range	Average	Std Dev	% Std Dev
97L1879-002 A	159	141-174	164	14	8.7
97L1879-002 B	172				
97L1879-002 C	141				
97L1879-002 D	174				
97L1879-002 E	173				

Table 5. Replicate sequential extraction data for Am-241.

SAMPLE	FRACTION	MASS OF SAMPLE (g)	MASS OF TRACER (g)	SPECIFIC ACTIVITY OF TRACER (Bq/g)	TRACER Bq ADDED	TRACER COUNTS	Am-241 COUNTS	Am-241 CNTS FROM TRACER	COUNT TIME (m)	SAMPLE ACTIVITY (Bq/G)	COUNTING UNCERT. (1σ)(Bq/G)	SAMPLE ACTIVITY (pCi/G)	COUNTING UNCERT. (1σ)(pCi/G)	DETECTOR EFFICIENCY	CHEMICAL YIELD %	AVERAGE ACTIVITY (pCi/G)	STD DEV ACTIVITY (pCi/G)	PERCENT STD DEV	PERCENT TOTAL ACTIVITY	SAMPLE SPECIFIC MDA (pCi/g)	RATIO Pu/Am
97L1879-002 F	Exchangable	2.943	1.0194	0.1796	0.1831	3229	40	5	1000	0.00067	0.00011	0.0181	0.0029	0.3152	93.3					0.0068	
97L1879-002 G	Exchangable	2.949	1.0065	0.1796	0.1808	3435	75	6	1000	0.00124	0.00014	0.0334	0.0039	0.3152	100.5					0.0063	
97L1879-002 H	Exchangable	3.048	1.0124	0.1796	0.1818	2155	18	4	1000	0.000400	0.000095	0.0108	0.0026	0.3152	62.7	0.021	0.012	55.7	0.043	0.0098	1.38
97L1879-002 F	Carbonate	2.943	1.0201	0.1796	0.1832	2172	978	4	1000	0.0279	0.0011	0.755	0.029	0.3152	62.7					0.0102	
97L1879-002 G	Carbonate	2.949	0.9827	0.1796	0.1765	2164	825	4	1000	0.02272	0.00093	0.614	0.025	0.3152	64.8					0.0098	
97L1879-002 H	Carbonate	3.048	1.0164	0.1796	0.1825	2296	1091	4	1000	0.0284	0.0010	0.766	0.028	0.3152	66.5	0.71	0.085	11.9	1.5	0.0092	0.52
97L1879-002 F	Sesquioxide	2.943	0.7227	6.8869	4.9772	40734	4706	67	1000	0.1926	0.0030	5.205	0.080	0.3152	43.3					0.0147	
97L1879-002 G	Sesquioxide	2.949	0.7234	6.8869	4.9820	40211	3375	66	1000	0.1390	0.0025	3.757	0.067	0.3152	42.7					0.0149	
97L1879-002 H	Sesquioxide	3.048	0.2077	6.8869	1.4304	11423	3965	19	1000	0.1621	0.0030	4.382	0.081	0.3152	42.2	4.45	0.73	16.3	9.2	0.0146	1.33
97L1879-002 F	Organic	2.943	0.5163	6.8869	3.5557	21106	19601	35	502	1.120	0.011	30.27	0.30	0.3152	62.5					0.0203	
97L1879-002 G	Organic	2.949	0.5228	6.8869	3.6005	18543	11831	31	450	0.7770	0.0091	21.00	0.25	0.3152	60.5					0.0233	
97L1879-002 H	Organic	3.048	0.5205	6.8869	3.5846	19791	15054	33	450	0.8926	0.0097	24.13	0.26	0.3152	64.9	25.13	4.72	18.8	52.2	0.0211	3.94
97L1879-002 F	Residual	2.943	0.5115	6.8869	3.5226	20724	13359	34	590	0.7696	0.0085	20.80	0.23	0.3152	52.7					0.0205	
97L1879-002 G	Residual	2.949	0.5129	6.8869	3.5323	23846	11612	39	590	0.5813	0.0066	15.71	0.18	0.3152	60.5					0.0178	
97L1879-002 H	Residual	3.048	0.5120	6.8869	3.5261	27393	14929	45	590	0.6286	0.0064	16.99	0.17	0.3152	69.6	17.83	2.65	14.8	37.0	0.0150	3.28
BLK 98-02	Exchangable	3.0109	1.0235	0.1796	0.1838	2903	35	5	1000	0.00064	0.00011	0.0172	0.0029	0.3152	83.5					0.0075	
BLK 98-02	Carbonate	3.0109	1.0164	0.1796	0.1825	2964	19	5	1000	0.000289	0.000066	0.0078	0.0018	0.3152	85.9					0.0072	
BLK 98-02	Sesquioxide	3.0109	0.3114	6.8869	2.1446	16137	26	27	1000	-0.0000276	-0.0000054	-0.00075	-0.00015	0.3152	39.8					0.0156	
BLK 98-02	Organic	3.0109	0.5174	6.8869	3.5633	21290	31	35	502	-0.000229	-0.000041	-0.0062	-0.0011	0.3152	62.9					0.0197	
BLK 98-02	Residual	3.0109	0.5148	6.8869	3.5454	26322	53	43	590	0.000428	0.000059	0.0116	0.0016	0.3152	66.5					0.0158	
97L1879-02 1-6	Total	1.0102	1.0327	6.8869	7.112	22115	4919	36	366	1.554	0.025	42.01	0.66	0.3152	44.9	43.8				0.1128	6.44
97L1879-02 1-7	Total	0.9774	1.0285	6.8869	7.083	26750	6271	44	366	1.687	0.024	45.59	0.64	0.3152	54.6					0.0960	
BLK 98-03	Total	0.9997	0.5158	6.8869	3.552	9819	31	16	366	0.0054	0.0010	0.145	0.026	0.3152	39.9					0.1282	

	Sum of Activity from fxns (pCi/G)	Range	Average	Std Dev	% Std Dev
97L1879-002 F	57	41-57	48	8	16.9
97L1879-002 G	41				
97L1879-002 H	46				

Table 6. Summary of reduction experiment results.

Pu-239/240 SOIL PARTITIONING DATA UNDER VARIOUS REDOX CONDITIONS

RFETS SAMPLE #	SAMPLE ALIQUOT NAME	MASS OF SAMPLE (G)	EXTRACTAN VOLUME (mL)	TRACER ADDED (Bq)	TRACER COUNTS	Pu-239/240 COUNTS		COUNT TIME (m)	SCALING FACTOR	SAMPLE ACTIVITY (pCi/g)	PERCENT OF TOTAL	SAMPLE ACTIVITY (Bq/L)	COUNTING UNCERT. (1σ)(Bq/L)	SAMPLE ACTIVITY (pCi/L)	COUNTING UNCERT. (1σ)(pCi/L)	DETECTOR EFFICIENCY	CHEMICAL YIELD %	SAMPLE SPECIFIC MDA (pCi/g)
97L1879-02	NR01	4.0594	400	5.1594	73271	1231		1000	0.95	0.607	0.37	0.2281	0.0066	6.17	0.18	0.3152	75.1	0.0065
	BLK 01	4.0226	400	0.3072	5955	74		1000	1	0.026		0.0095	0.0011	0.258	0.030	0.3152	102.5	0.0045
	BLK-12	4	400	0.306	5819	3		1000	1	0.001		0.0004	0.0002	0.0107	0.0062	0.3152	100.6	0.0047
97L1879-02	NR02	4.0392	400	0.9216	13217	337		1000	0.95	0.166	0.10	0.0618	0.0034	1.671	0.092	0.3152	75.8	0.0064
97L1879-02	NO02	4.001	400	0.6154	9599	1133		1000	0.95	0.516	0.32	0.1912	0.0060	5.17	0.16	0.3152	82.5	0.0060
	BLK-13	4	400	0.306	5301	55		1000	1	0.021		0.0079	0.0011	0.215	0.029	0.3152	91.6	0.0051
97L1879-02	NR04	4.1371	400	2.594	144952	1152		4000	0.835	0.161	0.10	0.0617	0.0018	1.668	0.049	0.3152	73.9	0.0018
97L1879-02	NR04 EL. SM	4.1371	400	0.3067	6630	6711		1500	1	2.028	1.24	0.776	0.013	20.98	0.36	0.3152	76.2	0.0040
97L1879-02	NR04 EL. LG	4.1371	400	0.3054	8144	3503		1500	1	0.858	0.52	0.328	0.0066	8.88	0.18	0.3152	94.0	0.0032
	BLK-14	4	400	2.6025	137698	165		4000	1	0.021		0.00780	0.00061	0.211	0.016	0.3152	69.9	0.0017

Am-241 SOIL PARTITIONING DATA UNDER VARIOUS REDOX CONDITIONS

RFETS SAMPLE #	SAMPLE ALIQUOT NAME	MASS OF SAMPLE (G)	EXTRACTAN VOLUME (mL)	TRACER ADDED (Bq)	TRACER COUNTS	Am-241 COUNTS	Am-241 IN TRACER	COUNT TIME (m)	SCALING FACTOR	SAMPLE ACTIVITY (pCi/g)	PERCENT OF TOTAL	SAMPLE ACTIVITY (Bq/L)	COUNTING UNCERT. (1σ)(Bq/L)	SAMPLE ACTIVITY (pCi/L)	COUNTING UNCERT. (1σ)(pCi/L)	DETECTOR EFFICIENCY	CHEMICAL YIELD %	SAMPLE SPECIFIC MDA (pCi/g)
97L1879-02	NR01	4.0594	400	7.056	99022	364	163	1000	0.95	0.100	0.23	0.0683	0.0036	1.84	0.10	0.3152	74.2	0.0065
	BLK 01	4.0226	400	0.1844	3016	22	5	1000	1	0.007	0.016	0.00336	0.00072	0.091	0.019	0.3152	86.5	0.0054
	BLK-12	4	400	0.1835	3256	10	5	1000	1	0.002	0.0040	0.00141	0.00045	0.038	0.012	0.3152	93.8	0.0050
97L1879-02	NR02	4.0392	400	0.363	4322	48	7	1000	0.95	0.024	0.0552	0.01061	0.0015	0.287	0.042	0.3152	63.0	0.0078
97L1879-02	NO02	4.001	400	0.363	5611	317	9	1000	0.95	0.142	0.3232	0.05397	0.0031	1.459	0.084	0.3152	81.7	0.0060
	BLK-13	4	400	0.306	5301	55	9	1000	0.95	0.019	0.0434	0.00835	0.0011	0.226	0.031	0.3152	91.6	0.0054
97L1879-02	NR04	4.0594	400	3.5378	180232	832	297	4000	0.835	0.084	0.19	0.0489	0.0017	1.322	0.046	0.3152	67.3	0.0021
97L1879-02	NR04 EL. SM	4.1371	400	0.09210	566	400	1	1500	1	0.424	1.0	0.1627	0.0106	4.398	0.287	0.3152	21.7	0.014
97L1879-02	NR04 EL. LG	4.1371	400	0.09104	2333	615	4	1500	1	0.156	0.36	0.0600	0.0027	1.622	0.074	0.3152	90.3	0.0033
	BLK-14	4	400	3.5371	170803	510	282	4000	1	0.032	0.07	0.0264	0.0012	0.714	0.032	0.3152	63.8	0.0018

Table 7. RFETS metals data.

RFETS SAMPLE	ALIQUOT NAME	SAMPLE FRACTION	SAMPLE MASS	METAL SYMBOL	MEAS. CONC. mg/L	ALIQUOT VOLUME (mL)	DILUTION VOLUME (mL)	INITIAL VOLUME (mL)	SAMPLE CONC. (mg/g)	%OF TOTAL	AVG % OF TOTAL
97L1879-02	A	Exchang.	3.0158	Ni	BDL	3	10	30	BDL		
97L1879-02	B	Exchang.	3.0163	Ni	BDL	3	10	30	BDL		
97L1879-02	C	Exchang.	3.0187	Ni	BDL	3	10	30	BDL		
97L1879-02	D	Exchang.	3.0127	Ni	BDL	3	10	30	BDL		
97L1879-02	E	Exchang.	3.0353	Ni	BDL	3	10	30	BDL		
97L1879-02	A	Exchang.	3.0158	Fe	0.039	3	10	30	0.0013	0.0071	
97L1879-02	B	Exchang.	3.0163	Fe	0.045	3	10	30	0.0015	0.0082	
97L1879-02	C	Exchang.	3.0187	Fe	0.031	3	10	30	0.0010	0.0057	
97L1879-02	D	Exchang.	3.0127	Fe	0.029	3	10	30	0.0010	0.0053	
97L1879-02	E	Exchang.	3.0353	Fe	0.023	3	10	30	0.0008	0.0042	0.0061
97L1879-02	A	Exchang.	3.0158	Mn	BDL	3	10	30	BDL		
97L1879-02	B	Exchang.	3.0163	Mn	BDL	3	10	30	BDL		
97L1879-02	C	Exchang.	3.0187	Mn	BDL	3	10	30	BDL		
97L1879-02	D	Exchang.	3.0127	Mn	BDL	3	10	30	BDL		
97L1879-02	E	Exchang.	3.0353	Mn	BDL	3	10	30	BDL		
97L1879-02	A	Exchang.	3.0158	Si	BDL	3	10	30	BDL		
97L1879-02	B	Exchang.	3.0163	Si	BDL	3	10	30	BDL		
97L1879-02	C	Exchang.	3.0187	Si	BDL	3	10	30	BDL		
97L1879-02	D	Exchang.	3.0127	Si	BDL	3	10	30	BDL		
97L1879-02	E	Exchang.	3.0353	Si	BDL	3	10	30	BDL		
97L1879-02	A	Exchang.	3.0158	Al	0.054	3	10	30	0.002	0.004	
97L1879-02	B	Exchang.	3.0163	Al	0.037	3	10	30	0.001	0.003	
97L1879-02	C	Exchang.	3.0187	Al	0.015	3	10	30	0.000	0.001	
97L1879-02	D	Exchang.	3.0127	Al	0.034	3	10	30	0.001	0.003	
97L1879-02	E	Exchang.	3.0353	Al	0.163	3	10	30	0.005	0.013	0.005
97L1879-02	A	Carbonate	3.0158	Ni	BDL	3	10	30	BDL		
97L1879-02	B	Carbonate	3.0163	Ni	BDL	3	10	30	BDL		
97L1879-02	C	Carbonate	3.0187	Ni	BDL	3	10	30	BDL		
97L1879-02	D	Carbonate	3.0127	Ni	BDL	3	10	30	BDL		
97L1879-02	E	Carbonate	3.0353	Ni	BDL	3	10	30	BDL		
97L1879-02	A	Carbonate	3.0158	Fe	0.545	3	10	30	0.018	0.100	
97L1879-02	B	Carbonate	3.0163	Fe	0.545	3	10	30	0.018	0.100	
97L1879-02	C	Carbonate	3.0187	Fe	0.414	3	10	30	0.014	0.076	
97L1879-02	D	Carbonate	3.0127	Fe	0.53	3	10	30	0.018	0.097	
97L1879-02	E	Carbonate	3.0353	Fe	0.345	3	10	30	0.011	0.063	0.087
97L1879-02	A	Carbonate	3.0158	Mn	0.605	3	10	30	0.020	5.4	
97L1879-02	B	Carbonate	3.0163	Mn	0.595	3	10	30	0.020	5.3	
97L1879-02	C	Carbonate	3.0187	Mn	0.535	3	10	30	0.018	4.8	
97L1879-02	D	Carbonate	3.0127	Mn	0.565	3	10	30	0.019	5.1	
97L1879-02	E	Carbonate	3.0353	Mn	0.594	3	10	30	0.020	5.3	5.2

RFETS SAMPLE	ALIQUOT NAME	SAMPLE FRACTION	SAMPLE MASS	METAL SYMBOL	MEAS. CONC. mg/L	ALIQUOT VOLUME (mL)	DILUTION VOLUME (mL)	INITIAL VOLUME (mL)	SAMPLE CONC. (mg/g)	%OF TOTAL	AVG % OF TOTAL
97L1879-02	A	Carbonate	3.0158	Si	3.353	3	10	30	0.11		
97L1879-02	B	Carbonate	3.0163	Si	2.766	3	10	30	0.09	See NOTE for total	
97L1879-02	C	Carbonate	3.0187	Si	2.724	3	10	30	0.09	silcon analysis data	
97L1879-02	D	Carbonate	3.0127	Si	3.251	3	10	30	0.11	below	
97L1879-02	E	Carbonate	3.0353	Si	1.822	3	10	30	0.06		
97L1879-02	A	Carbonate	3.0158	Al	1.2	3	10	30	0.04	0.094	
97L1879-02	B	Carbonate	3.0163	Al	0.98	3	10	30	0.03	0.077	
97L1879-02	C	Carbonate	3.0187	Al	0.89	3	10	30	0.03	0.070	
97L1879-02	D	Carbonate	3.0127	Al	1.2	3	10	30	0.04	0.094	
97L1879-02	E	Carbonate	3.0353	Al	0.80	3	10	30	0.03	0.062	4.5
97L1879-02	A	Sesquioxide	3.0158	Ni	0.058	3	10	30	0.0019	10	
97L1879-02	B	Sesquioxide	3.0163	Ni	0.056	3	10	30	0.0019	10	
97L1879-02	C	Sesquioxide	3.0187	Ni	0.057	3	10	30	0.0019	10	
97L1879-02	D	Sesquioxide	3.0127	Ni	0.061	3	10	30	0.0020	11	10.0
97L1879-02	E	Sesquioxide	3.0353	Ni	NA	3	10	30	NA	NA	
97L1879-02	A	Sesquioxide	3.0158	Fe	24.195	3	10	30	0.80	4.4	
97L1879-02	B	Sesquioxide	3.0163	Fe	23.96	3	10	30	0.79	4.4	
97L1879-02	C	Sesquioxide	3.0187	Fe	21.784	3	10	30	0.72	4.0	
97L1879-02	D	Sesquioxide	3.0127	Fe	24.568	3	10	30	0.82	4.5	
97L1879-02	E	Sesquioxide	3.0353	Fe	24.308	3	10	30	0.80	4.4	4.3
97L1879-02	A	Sesquioxide	3.0158	Mn	3.923	3	10	30	0.13	35	
97L1879-02	B	Sesquioxide	3.0163	Mn	3.785	3	10	30	0.13	34	
97L1879-02	C	Sesquioxide	3.0187	Mn	3.877	3	10	30	0.13	35	
97L1879-02	D	Sesquioxide	3.0127	Mn	4.049	3	10	30	0.13	36	
97L1879-02	E	Sesquioxide	3.0353	Mn	3.774	3	10	30	0.12	34	35
97L1879-02	A	Sesquioxide	3.0158	Si	22.4	3	10	30	0.74		
97L1879-02	B	Sesquioxide	3.0163	Si	20.5	3	10	30	0.68	See NOTE for total	
97L1879-02	C	Sesquioxide	3.0187	Si	21.6	3	10	30	0.72	silcon analysis data	
97L1879-02	D	Sesquioxide	3.0127	Si	21.9	3	10	30	0.73	below	
97L1879-02	E	Sesquioxide	3.0353	Si	NA	3	10	30	NA		
97L1879-02	A	Sesquioxide	3.0158	Al	10	3	10	30	0.33	0.78	
97L1879-02	B	Sesquioxide	3.0163	Al	9.5	3	10	30	0.31	0.74	
97L1879-02	C	Sesquioxide	3.0187	Al	9.2	3	10	30	0.30	0.72	
97L1879-02	D	Sesquioxide	3.0127	Al	9.6	3	10	30	0.32	0.75	
97L1879-02	E	Sesquioxide	3.0353	Al	9.8	3	10	30	0.32	0.76	0.75
97L1879-02	A	Organic	3.0158	Ni	0.13	3	10	15	0.0022	11	
97L1879-02	B	Organic	3.0163	Ni	0.103	3	10	15	0.0017	9	
97L1879-02	C	Organic	3.0187	Ni	0.134	3	10	15	0.0022	12	
97L1879-02	D	Organic	3.0127	Ni	0.089	3	10	15	0.0015	8	
97L1879-02	E	Organic	3.0353	Ni	0.171	3	10	15	0.0028	15	11

RFETS SAMPLE	ALIQUOT NAME	SAMPLE FRACTION	SAMPLE MASS	METAL SYMBOL	MEAS. CONC. mg/L	ALIQUOT VOLUME (mL)	DILUTION VOLUME (mL)	INITIAL VOLUME (mL)	SAMPLE CONC. (mg/g)	%OF TOTAL	AVG % OF TOTAL
97L1879-02	A	Organic	3.0158	Fe	13.7	3	10	15	0.23	1.3	
97L1879-02	B	Organic	3.0163	Fe	16.1	3	10	15	0.27	1.5	
97L1879-02	C	Organic	3.0187	Fe	13.1	3	10	15	0.22	1.2	
97L1879-02	D	Organic	3.0127	Fe	12.9	3	10	15	0.21	1.2	
97L1879-02	E	Organic	3.0353	Fe	16.6	3	10	15	0.27	1.5	1.3
97L1879-02	A	Organic	3.0158	Mn	0.868	3	10	15	0.014	3.9	
97L1879-02	B	Organic	3.0163	Mn	0.839	3	10	15	0.014	3.8	
97L1879-02	C	Organic	3.0187	Mn	0.886	3	10	15	0.015	4.0	
97L1879-02	D	Organic	3.0127	Mn	0.968	3	10	15	0.016	4.3	
97L1879-02	E	Organic	3.0353	Mn	0.923	3	10	15	0.015	4.1	4.0
97L1879-02	A	Organic	3.0158	Si	6.7	3	10	15	0.111		
97L1879-02	B	Organic	3.0163	Si	6.19	3	10	15	0.103	See NOTE for total	
97L1879-02	C	Organic	3.0187	Si	3.24	3	10	15	0.054	silcon analysis data	
97L1879-02	D	Organic	3.0127	Si	2.79	3	10	15	0.046	below	
97L1879-02	E	Organic	3.0353	Si	4.65	3	10	15	0.077		
97L1879-02	A	Organic	3.0158	Al	51	3	10	15	0.846	2.0	
97L1879-02	B	Organic	3.0163	Al	50	3	10	15	0.829	2.0	
97L1879-02	C	Organic	3.0187	Al	47	3	10	15	0.778	1.8	
97L1879-02	D	Organic	3.0127	Al	46	3	10	15	0.763	1.8	
97L1879-02	E	Organic	3.0353	Al	51	3	10	15	0.840	2.0	1.9

RFETS SAMPLE	ALIQUOT NAME	SAMPLE FRACTION	SAMPLE MASS	METAL SYMBOL	MEAS. CONC. mg/L	ALIQUOT VOLUME (mL)	DILUTION VOLUME (mL)	INITIAL VOLUME (mL)	SAMPLE CONC. (mg/g)	%OF TOTAL	AVG % OF TOTAL	
						Aliquot Vol. (mL)	Initial Vol. (mL)					
97L1879-02	3-1	Total	3.039	Ni	0.34	16.6	153.5		0.017			
97L1879-02	3-2	Total	3.0668	Ni	0.296	15.8	173.6		0.017			
97L1879-02	3-3	Total	3.3182	Ni	0.386	16.3	170.2		0.020			
97L1879-02	3-4	Total	3.3091	Ni	0.383	16.3	178.1		0.021			
97L1879-02	3-5	Total	3.0223	Ni	0.375	15.8	172.3		0.021			
97L1879-02	3-1	Total	3.039	Fe	333	16.6	153.5		17			
97L1879-02	3-2	Total	3.0668	Fe	283.000	15.8	173.6		16			
97L1879-02	3-3	Total	3.3182	Fe	376	16.3	170.2		19			
97L1879-02	3-4	Total	3.3091	Fe	356	16.3	178.1		19			
97L1879-02	3-5	Total	3.0223	Fe	342	15.8	172.3		19			
97L1879-02	3-1	Total	3.039	Mn	6.71	16.6	153.5		0.34			
97L1879-02	3-2	Total	3.0668	Mn	5.93	15.8	173.6		0.34			
97L1879-02	3-3	Total	3.3182	Mn	7.73	16.3	170.2		0.40			
97L1879-02	3-4	Total	3.3091	Mn	7.17	16.3	178.1		0.39			
97L1879-02	3-5	Total	3.0223	Mn	6.92	15.8	172.3		0.39			
97L1879-02	3-1	Total	3.039	Si	3.98	16.6	153.5		0.20			
97L1879-02	3-2	Total	3.0668	Si	3.98	15.8	173.6		0.23	NOTE: Si is volatilized		
97L1879-02	3-3	Total	3.3182	Si	3.9	16.3	170.2		0.20	during the digestion with		
97L1879-02	3-4	Total	3.3091	Si	4.78	16.3	178.1		0.26	hydrofluoric acid		
97L1879-02	3-5	Total	3.0223	Si	5.55	15.8	172.3		0.32			
97L1879-02	3-1	Total	3.039	Al	817	16.6	153.5		41			
97L1879-02	3-2	Total	3.0668	Al	671	15.8	173.6		38			
97L1879-02	3-3	Total	3.3182	Al	872	16.3	170.2		45			
97L1879-02	3-4	Total	3.3091	Al	823	16.3	178.1		44			
97L1879-02	3-5	Total	3.0223	Al	764	15.8	172.3		44			
97L1879-02	NR02		4.0392	Ni	0.027	10	378		0.0025	13		
97L1879-02	NO02		4.001	Ni	0.018	10	298		0.0013	7.0		
97L1879-02	NR04		4.1371	Ni	0.01	10	334		0.0008	4.2		
97L1879-02	NR02		4.0392	Fe	0.025	10	378		0.0023	0.013		
97L1879-02	NO02		4.001	Fe	0.098	10	298		0.0073	0.040		
97L1879-02	NR04		4.1371	Fe	0.015	10	334		0.0012	0.007		
97L1879-02	NR02		4.0392	Mn	0.058	10	378		0.0054	1.5		
97L1879-02	NO02		4.001	Mn	0.006	10	298		0.0004	0.12		
97L1879-02	NR04		4.1371	Mn	0.054	10	334		0.0044	1.2		
97L1879-02	NR02		4.0392	Al	0.03	10	378		0.0028	0.007		
97L1879-02	NO02		4.001	Al	0.156	10	298		0.0116	0.027		
97L1879-02	NR04		4.1371	Al	BDL	10	334		BDL	BDL		

Appendix 1. SOP: Total dissolution of solids for the radiochemical determinations of actinides, other non-volatile radionuclides and metals.

Place 1-3 grams of the prepared sample into an appropriate sized Teflon beaker. Add approximately 10mL of 1M nitric acid to allow carbonates to react. Add the appropriate yield tracers to the samples.

To each of the samples add 25 mL of concentrated nitric acid, 5 mL of concentrated hydrochloric acid and 25 mL of 48% hydrofluoric acid. Place a Teflon watch glass over each of the beakers.

Place the beakers on a hot plate at a temperature setting of 100-150 degrees Centigrade. Allow the digestion to proceed for at least twelve hours. Remove the samples from the hotplate and allow them to cool.

Add 10 mL of 48% hydrofluoric acid and return the samples to the hotplate uncovered. Increase the temperature to 200-250 degrees Centigrade. Allow the acids to evaporate until there is approximately 10 mL remaining. Repeat this sequence until the soil residue is minimal.

Add 10 mL of concentrated perchloric acid and 10 mL of hydrofluoric acid to each beaker. Turn the hotplate to a temperature of 400-450 degrees Centigrade. After the heavy white fumes of perchloric acid have evolved for several minutes, remove the sample from the hotplate to cool. Do not allow all of the acid to evaporate away.

Dilute the mixture with 2M nitric acid to a volume of approximately 50 mL. Transfer the solution to a 250 mL conical bottom centrifuge bottle. Rinse the beaker well with 2M nitric acid and transfer to the centrifuge bottle. Dilute the sample to approximately 150 mL with 2M nitric acid. Add 1 gram of solid boric acid to the samples and mix well. Proceed to the separation procedure.

Appendix 2: Selective Extraction followed by Separation Procedure of Plutonium and Americium in Rocky Flats Soils/Sediments.

Weigh out 3.0 +/- 0.1 grams of sediment into well sealing, 50 ml, conical bottom centrifuge tube.

Follow the extraction scheme as detailed in Yong *et al.* (1993) in the following manner:

Fraction 1) *Exchangeable Cations*

Add 8.0 mL of 1 M potassium nitrate to each of the samples. Cap the tubes and place them in a sealing plastic bag. Lay the bag containing the tubes on the shaker platform (Lab-line Instruments, Inc. Model # 4625) and turn the shaker to a setting of 3-4 to keep the sediment and extractant in motion. Allow the extraction to continue for eight hours.

After the prescribed extraction time, separate the extractant from the sediment by centrifugation (approximately 3500 rpm for 10 minutes) and decantation followed by filtration of the decanted liquid through a 0.45 micron membrane filter.

Determine the quantity of extractant left in the sediment by re-measuring the extractant recovered.

Rinse any residues on the filter back into the tube containing the majority of the sediment with approximately three times the quantity of residual extractant using D.I. water as the rinse.

Vortex the sample for several seconds, recentrifuge and filter the decanted supernate through a 0.45 micron membrane filter and combine with the extractant from this step.

Fraction 2) *Carbonates*

Pipette 8.0 mL of 1 M sodium acetate, that has been adjusted to pH 5 with acetic acid, into each of the sample residues from the first extraction. Cap the tubes and place them in a sealing plastic bag. Lay the bag containing the tubes on the shaker platform (Lab-line Instruments, Inc. Model # 4625) and turn the shaker to a setting of 3-4 to keep the sediment and extractant in motion. Allow the extraction to continue for five hours at room temperature.

After the prescribed extraction time, separate the extractant from the sediment by centrifugation (approximately 3500 rpm for 10 minutes) and decantation followed by filtration of the decanted liquid through a 0.45 micron membrane filter.

Determine the quantity of extractant left in the sediment by re-measuring the extractant recovered.

Rinse any residues on the filter back into the tube containing the majority of the sediment with

approximately three times the quantity of residual extractant using D.I. water as the rinse.

Vortex the sample for several seconds, recentrifuge and filter the decanted supernate through a 0.45 micron membrane filter and combine with the extractant from this step.

Fraction 3) *Oxides and hydroxides*

Add to the residues of extraction 2 20 mL of 0.04 M hydroxylamine hydrochloride in 25% (v/v) acetic acid at 96 +/- 3 degrees Centigrade, with occasional agitation, for six hours.

After the prescribed extraction time, separate the extractant from the sediment by centrifugation (approximately 3500 rpm for 10 minutes) and decantation followed by filtration of the decanted liquid through a 0.45 micron membrane filter.

Determine the quantity of extractant left in the sediment by re-measuring the extractant recovered.

Rinse any residues on the filter back into the tube containing the majority of the sediment with approximately three times the quantity of residual extractant using D.I. water as the rinse.

Vortex the sample for several seconds, recentrifuge and filter the decanted supernate through a 0.45 micron membrane filter and combine with the extractant from this step.

Fraction 4) *Bound to Organic Matter*

a) To the residue from extraction 3, add 3 mL of 0.02 M nitric acid and 5mL of 30% hydrogen peroxide that has been adjusted to a pH of 2 with nitric acid. Place the tubes in a water bath of 85 +/- 2 degrees Centigrade for two hours. Agitate the samples occasionally throughout the extraction period. Vent the tubes periodically so that excessive pressure does not build in the capped tubes. If necessary, leave the caps loose on the tubes so pressure does not build.

   After the prescribed extraction time, separate the extractant from the sediment by centrifugation (approximately 3500 rpm for 10 minutes) and decantation followed by filtration of the decanted liquid through a 0.45 micron membrane filter.

   Determine the quantity of extractant left in the sediment by re-measuring the extractant recovered.

   Rinse any residues on the filter back into the tube containing the majority of the sediment with approximately three times the quantity of residual extractant using D.I. water as the rinse.

   Vortex the sample for several seconds, recentrifuge and filter the decanted supernate through a 0.45 micron membrane filter and combine with the extractant from this step.

b) To the residue from step 4a add 3 mL of 30% hydrogen peroxide that has been adjusted to pH 2. Heat the samples to 85+/-2 degrees Centigrade for 3 hours with intermittent agitation.

After the prescribed extraction time, separate the extractant from the sediment by centrifugation (approximately 3500 rpm for 10 minutes) and decantation followed by filtration of the decanted liquid through a 0.45 micron membrane filter.

Determine the quantity of extractant left in the sediment by re-measuring the extractant recovered.

Rinse any residues on the filter back into the tube containing the majority of the sediment with approximately three times the quantity of residual extractant using D.I. water as the rinse.

Vortex the sample for several seconds, recentrifuge and filter the decanted supernate through a 0.45 micron membrane filter and combine with the original extractant.

To the residue from extraction 4b add 5mL of 3.2 M ammonium acetate in 20% (v/v) nitric acid. Dilute the mixture to 20 mL with D.I. water. Cap the tubes and place them in a sealing plastic bag. Lay the bag containing the tubes on the shaker platform (Lab-line Instruments, Inc. Model # 4625) and turn the shaker to a setting of 3-4 to keep the sediment and extractant in motion. Allow the extraction to continue for 30 minutes at room temperature.

After the prescribed extraction time, separate the extractant from the sediment by centrifugation (approximately 3500 rpm for 10 minutes) and decantation followed by filtration of the decanted liquid through a 0.45 micron membrane filter.

Determine the quantity of extractant left in the sediment by re-measuring the extractant recovered.

Rinse any residues on the filter back into the tube containing the majority of the sediment with approximately three times the quantity of residual extractant using D.I. water as the rinse.

Vortex the sample for several seconds, recentrifuge and filter the decanted supernate through a 0.45 micron membrane filter and combine with the extractant from this step.

Fraction 5) *Residual*

Spike the residue from fraction 4c with Pu-242 and Am-243 tracers and then digest with a 5:1 mixture of hydrofluoric acid and perchloric acid on a hotplate. Once the hydrofluoric acid has evaporated, the hotplate should be turned up until perchloric acid fumes begin to be

liberated. Allow the fumes to continue while on the hotplate for approximately 10-15 minutes before removing. Once the sample has cooled, add 1 gram of boric acid.

Spike the extractants from fractions 1-4 with a known amount of Pu-242 tracer and Am-243 tracer. Use approximately one-tenth the expected quantity of Pu-239/240 or Am-241 respectively in the entire extracted sediment. (e.g., a sample is 100 pCi/g Pu-239/240. A 3 gram extraction aliquot is taken. The Pu-242 tracer used should be 30 pCi for each extraction.)
For extractants 1-4:

Add 10 ml conc. nitric acid slowly. Allow to stand for several minutes at room temperature, then place on a warm hot plate for several minutes. Add a few drops of hydrogen peroxide to assist with the destruction of organic material, extractant residue and to assist in the exchange of tracer with the analyte.

Take the solution to dryness on a moderately hot hotplate. If it appears that the residue will not redissolve due to insoluble material, repeat the above treatment with nitric acid and hydrogen peroxide.

All samples:

Add 1-3 ml of conc. nitric acid and warm the solution on a hot plate.

Dilute the solution to 10-20 ml using 1M nitric acid.

Add 1 ml of 20 mg/ml Fe(III) carrier.

Add a spatula tip full of sodium nitrite crystals to the solution and mix well.

Allow the sample to stand for at least ten minutes.

Add conc. ammonium hydroxide in excess to precipitate the Fe carrier as iron hydroxide.

Centrifuge the sample for 5-10 minutes and discard the supernate.

Estimate the volume of the ferric hydroxide precipitate, add 4 times the volume of conc. hydrochloric acid and mix by vortexing. Add 9N hydrochloric acid to bring the solution to a final volume of 10-15 ml.

Fill a disposal plastic column (approximately 5mm I.D., 10 ml capacity) with 2 ml of AG 1X8 anion exchange resin. Cover the top of the resin with a small plug of glass wool.

Condition the resin with 10 ml of 9N hydrochloric acid. Discard the effluent.

Filter the solution onto the column if necessary.

Load the sample solution onto the column. Catch the column effluent as the Am fraction for further treatment.

Rinse the column with 1,2,5,10 ml successive rinses of 9N hydrochloric acid allowing each rinse to pass completely through before adding the next. Collect the effluent and combine with the Am fraction.

Rinse the column with an additional 40 mL of 9N hydrochloric acid and discard the effluent.

Rinse the column with 3 successive 5 ml portions of 0.5 N nitric acid. Collect these portions in a plastic test tube as the Pu fraction.

Pu Fraction

Add approximately 0.5 ml 30% hydrogen peroxide to the Pu portion and swirl.

Add 100 μg lanthanum carrier. Mix well. Add 5ml 25% HF. Mix well. Allow the sample to stand for at least 15 minutes.

Place a 25 mm 0.1 μm filter membrane in a filter funnel assembly and wet the membrane with a small amount of methanol or ethanol. Vacuum filter the solution then rinse with 10-15 ml of slightly basic water.

Remove the filter, dry at low heat, and mount on the planchet with double coated tape for APHA (alpha pulse height analysis).

Am Fraction

Evaporate the Am fraction (9N hydrochloric acid column effluent) to dryness on a hotplate.

Dissolve the residue in 3 mL of concentrated nitric acid. If the sample does not dissolve in 3 mL, continue adding nitric acid in 1 mL increments until residues dissolve. Heating may assist the dissolution process.

Once dissolved, add 15 mL of methanol for every 1 mL of concentrated nitric acid added.

Prepare an anion exchange column (1.5 cm I.D., 10 cm length) by adding a slurry of AG 1X8 100-200 mesh chloride form resin and twice the volume of 1N nitric acid/93% methanol to a height of 7cm in the column. Do not allow the column to dry out at any point in the procedure.

A funnel can be fitted onto the column to assist in the addition of the sample and rinses. If there are still visible residues in the sample, a filter can be utilized in the funnel to rid the solution of solids.

Condition the resin by rinsing the column with 40 mL of 1N nitric acid / 93% methanol solution.

Load the sample solution onto the column. After the sample has completely passed through the column, rinse the column with three successive 25 mL portions of 1N nitric acid / 93% methanol solution. The effluent can be properly disposed.

Elute the Am from the column by rinsing the column with three successive 20 mL portions of 8N nitric acid.

Evaporate the solution to dryness on a hotplate. Cool the sample.

Redissolve the sample in 10 mL of 2M ammonium thiocyanate / 0.1M formic acid solution. Allow the sample to dissolve for at least one hour. Physically mixing the sample may assist in the dissolution since the residues are small and adhere to the glass beaker.

Condition a TEVA Resin™ column by passing 5 mL of 2M thiocyanate / 0.1M formic acid solution through it.

Pass the sample solution through the column. Rinse the beaker and transfer the rinse to the column using 2 mL of 2M thiocyanate / 0.1M formic acid.

Rinse the column with two successive 5 mL portions of 1M thiocyanate / 0.1M formic acid solution.

Elute the Am from the column with 15 mL of 2N hydrochloric acid. Add 5 mL of concentrated nitric acid to the eluate and heat the solution to near dryness.

Add 1 mL of 8N nitric acid and heat the sample for approximately 5 minutes. Dilute the solution to 10 mL with D.I. water.

Add 100 µg lanthanum carrier. Mix well. Add 5ml 25% HF. Mix well. Allow the sample to stand for at least 15 minutes.

Place a 25 mm 0.1 µm filter membrane in a filter funnel assembly and wet the membrane with a small amount of methanol or ethanol. Vacuum filter the solution then rinse with 10-15 ml of slightly basic water.

Remove the filter, dry at low heat, and mount on a one inch planchet with double coated tape for APHA (alpha pulse height analysis).

Appendix 3. Quality assurance summary.

Precision

In all analysis types, precision is partially a function of the homogeneity of the sample, itself. Since the fundamental basis of the study is to determine association of the target actinides with the soil particulate matter, the samples could not be homogenized through the use of grinding and pulverization. The sample was thoroughly blended as described in section 2.1, but remained somewhat non-homogenous as indicated by the total dissolution data for the 3 gram and the 1 gram aliquots. Three to four gram samples were used in most analyses as a compromise between homogeneity issues and feasibility of the analytical procedures using larger aliquots. The precision data are presented as standard deviations of populations and are therefore a combination of all of the systematic and random uncertainties associated with the analyses. Wherever there is bias, however, such as is suspected with the analysis of the residual fraction for Pu, the uncertainty does not reflect the suspected bias.

Sequential Extraction

Five replicates were run using 3 grams of prepared soil for each. The percent standard deviation is a meaningful value to assess the precision of such a population. The two sigma (95% confidence interval) percent standard deviations for these data are as follows:

	Pu 239/240	Am-241
Exchangeable	46	111
Carbonate	17	24
Sesquioxide	25	33
Organic	24	38
Residual	31	30

Redox

Funding constraints disallowed the opportunity to perform duplicate analyses on the redox samples. Total uncertainties of the analytical data are estimated to be similar to those of the exchangeable fraction in the sequential analysis. Otherwise, the counting uncertainties are given in percentages as the two sigma (95% confidence interval) uncertainty:

TPU Sample	% TPU / %counting Unc. Pu-239/240		%TPU / % counting Unc. Am-241	
NR01	46	6	111	11
NR02	46	11	111	31
NR04	46	6	111	12
NO02	46	6	111	12
NO03 (0.45 um)	46	3	111	9
NO03 (10K MW)	46	4	111	18

Total Dissolution

The precision data of Pu-239/240 for 3 gram aliquots of soil performed on five replicates is represented by percent standard deviation of the population at the 95% confidence interval. Am-241 analysis was not performed on these replicates.

Samples	Pu-239/240
3-1,2,3,4,5	36

The precision data for Pu-239/240 and Am-241 for the total dissolution of 1 gram of soil is given by the Duplicate Error Ratio, F/E (as defined in RFETS SOW Isotopic Determinations by Alpha Spectrometry, Module RC01-B.2) of sample 1-6 and 1-7. Based upon the replicate analyses performed for 3 gram samples, the TPU (total propagated uncertainty at the 95% confidence interval) of the values is estimated at 36%. Thus, the DER is calculated using these uncertainties.

Sample	DER Pu-239/240	DER Am-241
1-6 & 1.7	0.6	0.16

Accuracy

As specified in the Quality Assurance Plan, all sample specific (posteriori) MDA's for these analyses have been met. MDA calculations are performed using the formula given in RFETS Module RC01-B.2 section 5.2. A conservative background count of 5 is utilized in each case. The actual backgrounds were monitored to less than this conservative value. In every case, activity above the MDA is demonstrated and the analytical uncertainty becomes the value of interest as indicated in ANSI Standard N42.23. MDA as an *a priori* concept is of no value to these *posteriori* data.

Sequential Extraction

Pu-239/240

The accuracy of these data can only be assessed on the basis of data comparison since there is really no "known" or "true" value. The favorable comparison to previous data for similar type extractions is evidence of accurate analytical results. However, it should be noted that there are differences in the extraction schemes of this work and that performed earlier by Litaor, *et al.* We believe that the residual phase data in the results of this study are biased low. (The sum of the fractions is significantly less than the average total activity) The cause is somewhat unknown, but is speculated to be due to the incomplete dissolution and tracer exchange for the residual phase extraction as detailed in the appendix. We are analyzing another set of replicates using a more rigorous technique for the residual phase assay.

Tracer recoveries are generally high, with 77% of the results having chemical yields grater than 75%. 63% of the chemical yields are greater than 90%. Only 3 results (10%) fall below 50% chemical yield, and all of the results are greater than 20%. Of the 2 sample results that have chemical yields less than 50%, both activity results are slightly higher than the other four results in their respective data sets. However, the slight bias has minimal effect upon the average activity.

Sequential extractions for Pu-239/240 were in progress or complete prior to the decision to include blank spikes as documented in the 1998 Quality Assurance Plan. Therefore, blank spikes were not performed for these analyses.

Blanks for the sequential extractions of Pu-239/240 are assessed here on the basis of the percentage of the activities in the respective fraction. The blank for the exchangeable fraction is a significant percentage (34%) of the average activity obtained in that fraction. Due to the high levels of activity in the samples and the inability to isolate the high level activity from the low level activity in shared apparatus of the procedure, it is not surprising to have contamination at these levels. This low level of contamination (0.01 pCi/g) is reflected in the elevated percent standard deviation (46% at the 95% confidence interval) of the exchangeable fraction.

Am-241

The chemical yields are generally lower than the Pu-239/240 results, which is anticipated due to the complexity of the Am analysis. 80% of the results have chemical yields greater than 50%. Of the results that fell below 50%, the data are in good agreement with the replicates and do not present cause for reanalysis or a situation of unusable data.

Blanks for the sequential extractions of Am-241 are assessed here on the basis of the percentage of the activities in the respective fraction. The blank for the exchangeable fraction is a significant percentage (81%) of the average activity obtained in that fraction. Due to the high levels of activity in the samples and the inability to isolate the high level activity from the low level activity in shared apparatus of the procedure, it is not surprising to have contamination at these levels. This low level of contamination (0.02 pCi/g) is reflected in the elevated percent standard deviation (111% at the 95% confidence interval) of the exchangeable fraction. Percent of average activity for the other fractions is 1% or less.

A Laboratory Control Sample (LCS), also referred to as a blank spike, was analyzed with the sequential extraction of Am-241. The data are shown on the "QC Data" Spreadsheet. As predictable, the majority of the activity is released in the first fractions, since the activity has been added as in soluble form and the blank matrix is a clean quartz silica sand providing little substrate for adsorption of the analyte. As indicated in the spreadsheet, the sum of the fractions is 99% of the analyte activity added to the blank spike.

Redox

The accuracy of the redox data is difficult to assess due to the experimental nature of the analysis. The accuracy is essentially defined by the procedure. Nonetheless, certain criteria that have been met suggest that the analyses were performed correctly.

Pu-239/240

Chemical yields are high and within acceptable limits indicating that the chemical separations and analyses are performed correctly.

Recovery of the spiked analyte in the matrix spike samples (shown in the "QC DATA" spreadsheet) is very low indicating that the analyte is binding in some manner to the matrix soil. This is highly predictable and supports the data obtained in the sequential extractions.

Blanks are generally a small percentage of the sample activities and are within acceptable limits for these data.

Am-241

Chemical yields are within acceptable limits indicating that the chemical separations and analyses are performed correctly. The yields are lower than the Pu yields which is typical due to the added complexity of separating and purifying Am.

Recovery of the spiked analyte in the Matrix Spike samples (shown in the "QC DATA" spreadsheet) is very low indicating that the analyte is binding in some manner to the matrix soil. This is highly predictable and supports the data obtained in the sequential extractions.

Blanks are generally a small percentage of the sample activities and are within acceptable limits for these data.

Blank 14 shows some significant Am-241 contamination (0.02 pCi/L). It is a significant fraction of the activity extracted from the sample. However it must be remembered that the extract from the sample is only 0.19% of the activity of the sample. In addition, the Am-243 tracer contains a small percentage of Am-241 contamination. It is estimated to be 0.165% of the tracer activity, but there is an uncertainty about that figure. If it were roughly twice the estimated percentage, it would account for the contamination in Blank 14. Since this blank was traced with a

high level of Am-243 to match the level that the sample was traced, the contamination could readily be attributed to the tracer contamination.

Representativeness

A chain of custody form was received and retained for sample 97L1879-002 during fiscal year 1997.

Work plans were approved by the Site and followed.

Comparability

Established analytical methods were used.

All analytical/radiochemistry protocols are documented and/or referenced.

Completeness

The number of samples analyzed (both real and QC) match the work plan except for noted exceptions as documented in the "Anomalous Occurrences" portion of this QA/QC section.

Anomalous Occurrences

Am data for the sequential extraction analyses were not obtained from the same aliquots as the Pu data. This is the result of an analytical error in the processing of the Am fraction for the original set of aliquots A-E. The effluents from the Pu separation anion exchange columns should be caught independently for further processing of the Am fraction. We had been processing only Pu fractions and was accustomed to collecting the effluents in a single container for disposal. Once these effluents were combined for the first two fractions (exchangeable and carbonate), it was determined that independent Am analyses were preferable to obtaining only partial Am data from the same aliquots. Thus, independent aliquots, F-H, were used to obtain Am data for the sequential extractions.

Upon thorough review of the Am count data for the organic and sesquioxide fractions of sample aliquots F and G, it was determined that an error had been made in the tracer spiking records. The records did indicate that an error had been made and there was some question about the destination of two additions of Am-243 tracing solution (tracer). Once the count data and the log book were rectified along with the knowledge of the analyst the scenario became obvious as follows:

While intending to add tracer to the residual fraction of samples F and G, the analyst mistakenly added tracer to the sesquioxide fraction of samples F and G which had already had tracer added. Aware that it was not the residual samples that had been spiked, the analyst then properly spiked and recorded the amount added to the residual fraction. The analyst then mistakenly recorded the aforementioned second spiking of the sesquioxide fraction as having been added to the organic fraction. Once the count data were reviewed for tracer recovery, it was obvious (due to unattainably large recoveries in that the two tracer additions were contained in the sesquioxide fraction of aliquots F and G and not the organic fraction. The final report contains the corrected data and any previous versions of the report should be considered erroneous. Raw count data and log book spiking records are retained, and copies will accompany the final report for the study upon its completion, that will substantiate and justify the corrections made in these Am data.

As discussed in section 2.6 of this document, the configuration, cost, and time (3-4 weeks per sample) for running multiple analyses for the reduction experiments poses serious limitations on the feasibility of performing the usual quality control measures (duplicates, spikes, and matrix spikes) for routine analytical protocol. Quality control measures were performed that were feasible under the constraints mentioned and are included for review. Data have been collected (blanks and control samples) that will add to the defensibility of the data. Duplicate analyses

may still be performed if determined by the 1999 Workscope document as a priority given the known analytical time and monetary constraints of the study.

As indicated in the specific analytical portions of this section, samples with tracer recoveries of less than 50% were not reanalyzed. The data quality objectives were not adversely affected by these lower recoveries due to the fact that the individual data were a part of a population of data that supported the individual results. The value of reanalysis in these cases was determined to be minimal.

The ICP analysis of Si in the total digestion and in the residual fraction of the selective extraction is of no value since in the digestion procedure Si is volatilized with the use of hydrofluoric acid at high temperatures. Therefore, the mass balance between summing the Si from the fractions and comparing to the total Si is not valid.

The mass of soil particulate removed with each reduction potential measurement introduces a small, immeasurable bias in the final result of the solubilized Pu from the reduction extraction experiments. The value of 0.0397 grams of particulate removed per measurement was derived from pre-weighing 10 filter disks prior to sampling and then re-weighing the ten disks after a drying period. If twenty measurements are made throughout the course of the reduction phase, approximately 0.8 grams or 20% of particulate will have been removed by the termination of the reduction period. The majority of these measurements (>90%) are made after the target reduction potential has been reached. Since the kinetics of the Pu release are unknown, the effect of the removal of this material is unknown and unquantifiable. There is an upper bound which limits the effect to a Pu value 20% higher than that obtained but is likely a much smaller effect, probably less than 5%.

QC DATA

(EXCEPT BLANKS SHOWN WITH SAMPLE DATA)

SAMPLE DESCRIPT.	SAMPLE NAME	ISOTOPE	FRACTIO	MASS OF TRACER (g)	SPECIFIC ACTIVITY OF TRACER (Bq/g	TRACER ADDED (Bq)	MASS OF ANALYTE (g)	SPECIFIC ACTIVITY OF ANALYTE (Bq/g)	ANALYTE ADDED (Bq)	TRACER COUNTS	ANALYTE COUNTS	ANALYTE CNTS FROM TRACER	COUNT TIME (m)	ANALYTE ACTIVITY (Bq/G)	COUNTING UNCERT. (1s)(Bq/G)	ACTIVITY OF SPIKED ANALYTE	PERCENT RECOVERY OF SPIKE	DETECTOR EFFICIENCY	CHEMICAL YIELD %
REDOX SAMPLES																			
97L1879-02 AMBIENT	NCS01	Pu	NA	1.0858	0.2823	0.3065	4	0	0.000	5632	1049	0	1000	0.01427	0.00048	NA	NA	0.3152	97.2
97L1879-02 AMBIENT SPIKE	SCS01	Pu	NA	1.0844	5.0371	5.4622	4.2309	1.436	6.076	115174	3837	0	1000	0.04301	0.00071	0.0287	0.47	0.3152	111.5
97L1879-02 AMBIENT	NCS01	Am	NA	1.0188	0.1796	0.1830	2	0	0.000	2981	107	5	1000	0.00313	0.00031	NA	NA	0.3152	86.1
97L1879-02 AMBIENT SPIKE	SCS01	Am	NA	1.0252	6.8869	7.0604	2.0614	1.5237	3.141	140002	790	231	1000	0.01368	0.00049	0.0105	0.34	0.3152	104.8
TOTAL DIGESTIONS																			
SAND BLANK SPIKE	LCS 1	Pu	NA	1.077	0.2823	0.3040	1.0511	1.436	1.509	4294	25099	0	1000	1.691	0.02792	1.691	112	0.3152	74.7
SAND BLANK SPIKE	LCS 3	Pu	NA	0.5453	4.7587	2.5949	1.0656	1.436	1.530	12681	7767	0	592	1.492	0.02149	1.492	97.5	0.3152	43.6
SAND BLANK SPIKE	LCS 3	Am	NA	0.5157	6.8869	3.5516	1.0306	1.524	1.571	10101	4004	17	366	1.360	0.02540	1.360	86.6	0.3152	41.1
SEQUENTIAL EXTRACTIONS																			
SAND BLANK SPIKE	LCS 2	Am	EXCHANG.	1.0217	0.1796	0.1835	1.0217	1.5237	1.557	2803	18698	5	1000	1.198	0.024	1.198	76.9	0.3152	80.8
SAND BLANK SPIKE	LCS 2	Am	CARBONAT	1.0193	0.1796	0.1831	1.0217	1.5237	1.557	2373	3292	4	1000	0.2483	0.0067	0.248	15.9	0.3152	68.5
SAND BLANK SPIKE	LCS 2	Am	SESQUIOX.	0.2087	6.8869	1.4373	1.0217	1.5237	1.557	8818	511	15	502	0.0792	0.0036	0.079	5.1	0.3152	64.6
SAND BLANK SPIKE	LCS 2	Am	ORGANIC	0.5174	6.8869	3.5633	1.0217	1.5237	1.557	18457	115	30	450	0.0160	0.0015	0.016	1.0	0.3152	60.9
SAND BLANK SPIKE	LCS 2	Am	RESIDUAL	0.5126	6.8869	3.5302	1.0217	1.5237	1.557	43333	157	71	926	0.00682	0.00055	0.007	0.4	0.3152	70.1
															SUM OF FRACTIONS		99.4		

Appendix 4. Raw ICP/AE Data.

Analysts: Laura Brubaker and Jessica Jordet
Method: NewWaters w/Internal Std and MSF

Date: 7/14/98
Remarks: All concentrations given in mg/L
BDL signifies concentrations below detection level

Analyte	soil blank 98-01 organic	002A organic	002B organic	002C organic	002D organic	002E organic	soil blank 98-01 o/h
Ag 328.068	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Al 308.215	16.713	50.878	50.487	47.210	46.038	50.727	7.869
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.773	0.419	0.784	0.297	0.362	0.375	0.212	0.211
Ba 455.403	0.549	0.589	0.584	0.556	saturated	0.603	0.670
Be 313.107	BDL	BDL	BDL	0.001	0.002	0.001	0.037
Ca 317.933	14.095	18.526	16.293	18.574	16.148	16.470	27.105
Cd 214.438	BDL	0.004	0.005	0.004	0.004	0.004	0.040
Co 228.616	BDL	BDL	BDL	BDL	BDL	BDL	0.090
Cr 205.552	0.036	0.291	0.203	0.328	0.153	0.224	0.042
Cu 324.754	0.065	0.118	0.076	0.074	0.072	0.095	0.137
Fe 238.204	2.351	13.703	16.101	13.145	12.928	16.662	34.318
K 766.491	7.557	14.943	15.736	15.478	16.402	16.358	25.083
Li 670.781	0.029	0.048	0.046	0.039	0.039	0.039	0.097
Mg 279.553	5.120	5.529	6.046	5.569	5.709	5.742	10.056
Mn 257.610	0.857	0.868	0.839	0.886	0.968	0.923	3.397
Mo 202.030	0.012	0.012	0.008	0.025	BDL	0.007	0.064
Na 589.592	2.222	4.579	4.048	4.483	6.027	5.210	56.143
Ni 231.604	0.038	0.130	0.103	0.134	0.089	0.171	0.158
P 177.434	0.770	6.273	5.674	3.753	4.109	5.473	4.487
Pb 220.353	0.045	0.624	0.669	0.601	0.639	0.628	0.238
S 180.669	1.081	9.581	8.890	9.690	9.383	9.578	0.387
Sb 217.581	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Si 251.611	4.749	6.698	6.191	3.238	2.785	4.653	18.395
Sn 189.933	0.017	BDL	BDL	BDL	BDL	BDL	0.074
Sr 407.771	0.068	0.057	0.051	0.052	0.052	0.053	0.181
Ti 334.941	0.265	1.519	1.433	0.544	0.527	1.415	0.004
V 292.402	0.078	0.224	0.223	0.226	0.221	0.230	0.142
Zn 213.856	0.156	0.083	0.092	0.088	0.079	0.141	1.124
Sc 361.384	0.968	0.967	1.009	1.114	1.087	1.147	0.597

Appendix 4. Raw ICP/AE Data.

Analysts:
Method:

Analyte	002A o/h	002B o/h	002C o/h	002D o/h	002E o/h	soil blank 98-01 exchan.	002A exchangeable
Ag 328.068	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Al 308.215	9.976	9.537	9.187	9.648	9.802	0.411	0.054
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.773	0.121	0.100	0.193	0.161	0.262	saturated	saturated
Ba 455.403	0.564	0.544	0.545	0.532	0.547	0.410	0.738
Be 313.107	0.006	0.005	0.005	0.006	0.006	BDL	BDL
Ca 317.933	34.579	34.915	37.899	35.003	33.763	32.587	54.352
Cd 214.438	0.019	0.017	0.017	0.018	0.017	BDL	BDL
Co 228.616	0.067	0.065	0.065	0.067	0.065	BDL	BDL
Cr 205.552	0.008	BDL	BDL	BDL	0.061	BDL	BDL
Cu 324.754	0.016	0.006	0.009	0.006	0.010	0.002	BDL
Fe 238.204	24.195	23.960	21.784	24.568	24.308	0.889	0.024
K 766.491	36.082	35.774	39.193	38.346	36.696	2600.717	2707.566
Li 670.781	0.041	0.036	0.037	0.041	0.042	0.006	BDL
Mg 279.553	4.281	4.053	4.135	4.493	3.990	5.098	1.804
Mn 257.610	3.923	3.785	3.877	4.049	3.774	0.002	BDL
Mo 202.030	BDL	0.008	0.012	0.008	0.005	BDL	BDL
Na 589.592	72.838	69.454	75.246	77.844	0.088	7.957	2.972
Ni 231.604	0.058	0.056	0.057	0.061	67.272	BDL	BDL
P 177.434	1.159	1.383	1.516	1.518	0.562	2.115	1.716
Pb 220.353	0.413	0.427	0.410	0.417	0.092	BDL	BDL
S 180.669	1.134	0.971	1.059	1.119	1.270	0.768	0.566
Sb 217.581	BDL	BDL	BDL	BDL	0.415	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	0.999	BDL	BDL
Si 251.611	22.425	20.529	21.624	21.907	BDL	0.855	0.672
Sn 189.933	0.027	0.072	0.070	0.064	BDL	BDL	BDL
Sr 407.771	0.070	0.065	0.070	0.068	21.096	BDL	0.162
Ti 334.941	0.004	0.008	0.040	0.008	0.089	0.023	BDL
V 292.402	0.090	0.087	0.086	0.089	0.067	BDL	BDL
Zn 213.856	0.440	0.414	0.426	0.424	0.024	0.015	0.007
Sc 361.384	1.196	1.327	1.318	1.292	1.256	1.013	1.014

Appendix 4. Raw ICP/AE Data.

Analyte	002B exchangeable	002C exchangeable	002D exchangeable	002E exchangeable	soil blank 98-01 carbo	002A carbonates
Ag 328.068	BDL	BDL	BDL	BDL	BDL	BDL
Al 308.215	0.037	0.015	0.034	0.163	0.545	1.218
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL
B 249.773	saturated	saturated	saturated	saturated	saturated	saturated
Ba 455.403	0.741	0.716	0.753	0.735	0.432	0.429
Be 313.107	BDL	BDL	BDL	BDL	BDL	BDL
Ca 317.933	54.864	53.194	55.361	53.622	189.661	105.693
Cd 214.438	BDL	BDL	BDL	BDL	0.001	0.005
Co 228.616	BDL	BDL	BDL	BDL	BDL	BDL
Cr 205.552	BDL	BDL	BDL	BDL	0.021	BDL
Cu 324.754	BDL	0.002	0.001	0.001	0.009	0.006
Fe 238.204	0.045	0.031	0.029	0.023	0.053	0.545
K 766.491	2625.566	2551.279	2652.162	2554.008	195.705	267.495
Li 670.781	BDL	BDL	BDL	BDL	0.010	0.012
Mg 279.553	1.816	1.774	1.852	1.790	5.341	1.995
Mn 257.610	BDL	BDL	BDL	BDL	0.470	0.605
Mo 202.030	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	2.919	3.030	3.310	3.181	saturated	saturated
Ni 231.604	BDL	BDL	BDL	BDL	0.007	BDL
P 177.434	1.148	1.009	1.036	1.006	8.016	6.872
Pb 220.353	BDL	BDL	BDL	BDL	BDL	0.026
S 180.669	0.534	0.549	0.566	0.538	3.203	0.962
Sb 217.581	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	BDL	BDL
Si 251.611	0.048	BDL	BDL	BDL	0.576	3.353
Sn 189.933	BDL	BDL	BDL	0.027	BDL	BDL
Sr 407.771	0.162	0.157	0.164	0.160	0.453	0.147
Ti 334.941	BDL	BDL	BDL	BDL	0.005	0.030
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL
Zn 213.856	0.009	0.008	0.008	0.008	0.732	0.064
Sc 361.384	1.051	1.068	1.060	1.066	1.003	0.954

Appendix 4. Raw ICP/AE Data.

Analyte	002B carbonates	002C carbonates	002D carbonates	002E carbonates	97L1879-02 3-1	97L1879-02 3-2
Ag 328.068	BDL	BDL	BDL	BDL	BDL	BDL
Al 308.215	0.977	0.886	1.153	0.802	817.053	670.828
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL
B 249.773	saturated	saturated	saturated	saturated	saturated	saturated
Ba 455.403	0.433	0.461	0.433	0.440	8.801	7.382
Be 313.107	BDL	BDL	BDL	BDL	0.049	0.006
Ca 317.933	110.412	125.645	102.942	102.777	214.027	162.746
Cd 214.438	0.005	0.005	0.005	0.005	0.052	0.043
Co 228.616	BDL	BDL	BDL	BDL	0.187	0.162
Cr 205.552	BDL	BDL	BDL	BDL	0.559	0.490
Cu 324.754	0.004	0.003	0.005	0.005	0.228	0.193
Fe 238.204	0.545	0.414	0.530	0.345	332.979	282.763
K 766.491	282.662	318.430	292.615	286.075	350.981	287.472
Li 670.781	0.012	0.013	0.013	0.012	0.433	0.340
Mg 279.553	1.913	2.184	1.880	1.803	58.797	52.102
Mn 257.610	0.595	0.535	0.565	0.594	6.707	5.930
Mo 202.030	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	saturated	saturated	saturated	saturated	saturated	689.319
Ni 231.604	BDL	BDL	BDL	BDL	0.340	0.296
P 177.434	3.686	4.707	4.134	3.409	49.357	41.876
Pb 220.353	0.027	0.026	0.033	0.037	0.762	0.669
S 180.669	0.978	1.126	0.943	1.002	7.539	6.057
Sb 217.581	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	BDL	BDL
Si 251.611	2.766	2.724	3.251	1.822	3.976	3.983
Sn 189.933	BDL	BDL	BDL	BDL	BDL	BDL
Sr 407.771	0.145	0.169	0.140	0.142	2.277	1.856
Ti 334.941	0.009	0.205	0.014	0.338	40.320	33.445
V 292.402	BDL	BDL	BDL	0.010	0.986	0.821
Zn 213.856	0.069	0.070	0.055	0.133	1.150	0.992
Sc 361.384	1.094	1.057	1.045	1.057	1.024	1.082

Analyte	97L1879-02 3-3	97L1879-02 3-4	97L1879-02 3-5	NOO2	NR02	NR02B
Ag 328.068	BDL	BDL	BDL	BDL	BDL	BDL
Al 308.215	871.900	823.029	764.091	0.156	0.030	0.184
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL
B 249.773	saturated	saturated	3346.904	0.032	0.029	0.047
Ba 455.403	9.257	8.745	9.472	0.093	0.112	0.140
Be 313.107	0.009	0.007	0.004	BDL	BDL	BDL
Ca 317.933	209.868	207.784	199.219	17.974	19.623	17.135
Cd 214.438	0.058	0.058	0.049	BDL	0.007	0.010
Co 228.616	0.212	0.211	0.183	BDL	BDL	BDL
Cr 205.552	0.660	0.644	0.559	BDL	BDL	BDL
Cu 324.754	0.247	0.249	0.226	0.003	0.045	0.034
Fe 238.204	375.733	354.573	341.841	0.098	0.025	0.111
K 766.491	359.717	344.740	309.338	31.299	43.286	532.531
Li 670.781	0.437	0.413	0.419	BDL	BDL	BDL
Mg 279.553	66.861	67.019	61.262	0.623	0.625	0.675
Mn 257.610	7.726	7.172	6.921	0.006	0.058	0.031
Mo 202.030	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	saturated	saturated	saturated	0.228	13.952	12.878
Ni 231.604	0.386	0.383	0.375	0.018	0.027	0.042
P 177.434	50.430	47.175	24.878	BDL	BDL	2.469
Pb 220.353	0.893	0.843	0.778	BDL	BDL	BDL
S 180.669	8.446	8.137	7.247	1.761	1.705	3.284
Sb 217.581	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	BDL	BDL
Si 251.611	3.903	4.775	5.550	2.216	2.013	2.210
Sn 189.933	BDL	BDL	BDL	BDL	BDL	BDL
Sr 407.771	2.429	2.264	2.202	0.038	0.040	0.034
Ti 334.941	45.149	43.115	42.221	0.019	0.015	0.018
V 292.402	1.097	1.057	0.973	BDL	BDL	BDL
Zn 213.856	1.314	1.245	1.228	0.026	0.039	0.040
Sc 361.384	1.119	1.080	1.001	1.149	1.085	1.061

Rocky Flats Environmental Technology Site
Actinide Migration Studies
Meetings: October 21-22, 1998
Advisory Group: Greg Choppin, David Clark, David Janecky, Kirk Nordstrom

Summary and recommendations for path forward

Particulate transport continues to be the dominant transport pathway identified for the Pu and Am actinides off the Site, based on surface water characterization, soil redox reaction process experiments and erosion modeling. Experimental plans for characterization of redox processes, of surface water, and of site end-state concepts were presented and discussed. Microbiologic processes coupled to redox reactions in soils and an approach to define experimental constraints were also discussed, including cognizant experts to be contacted during definition of a detailed experimental plan. Use of a K_d approach for the Site as the overall summary of quantitative measures for risk and release calculations was discussed extensively. We have included in this report our present evaluation of the limitations and caveats of such an approach in application to the complicated and nonlinear process of actinide migration at Rocky Flats Environmental Technology Site.

Recently completed uranium isotopic analysis results were presented for selected solar ponds plume and background samples. This work has significantly enhanced characterization of the contamination problem, and replaced simplified assumptions with quantitative data. Coupled with these improvements in characterization, the geochemical modeling effort needs to define tests for our geochemical and transport understanding.

We heard discussion of end-state planning and concepts, including removal of the retention ponds and re-engineering the drainage. At this time, it remains unclear if site cleanup and the conceptual end-state will remove the problem of surface-water exceedances at the Site boundary. The impact and detailed operations of wetlands versus settling ponds is not clear, given the present understanding of contaminant distribution and transport via surface water. The Site might need to consider not removing ponds in some or all instances, and potential enhancement of surface water quality through reconfiguration or addition of ponds at other locations.

Progress and integration

Characterization of redox processes, chemical/physical contaminant signatures (Pu and Am concentrations and ratios; U isotopics) and erosion modeling have advanced during the past year. Definition of workscope for FY99 includes substantial opportunities for integration (as noted below). Integration and application of results should be a focus of AMS discussions during the year to maximize their value in application to site problems.

Results presented

Bruce Honeyman – soil/solution redox reactions and actinide mobility characterization.

Peter Santschi – surface water actinide component size fractionation and characterization.

Craig Cawdry – uranium isotopic analyses of groundwater samples from the solar ponds plume and background sites.

Plans presented and discussed

Mike Peters – RFETS closure project plans and end-state summary.

Keith Motyl – RFETS surface water and end-state.

Greg Wetherbee – End-state roadmap and FY99 plans.

Discussion of FY99 efforts

Redox Studies.

The committee found the development and application of an electrochemical cell and use of redox indicators to be a very important study that goes a long way towards answering key questions of importance to the Site. These studies indicate that the "operational" solubility of plutonium appears to decrease, while the solubility of americium is unchanged under strongly reducing conditions. "Operational" solubility is defined as that measured in solution after using a filter sized to separate particulates, while recognizing that small particulates are expected to be within the filtrate. It is stressed that these observation are only preliminary, and need to be confirmed or revised by determination of additional data points below +164 mV and between +164 to +800 mV during the upcoming FY. Intermediate Eh points where Mn and SO_4/H_2S redox reactions occur in C-2 pond and soils should be examined, and the work should be augmented with some redox state modeling.

The preliminary results suggest that reducing conditions decrease the amount of plutonium in the cell. It is unclear at this time whether this is the result of precipitation, hydrolysis, sorption, or some other chemical reactions. However, it is well known that Pu(V) is a predominant oxidation state for plutonium in dilute ground water environments. Pu(V) has a rather low charge-to-size radius ratio, and is known to form only weak complexes with ligands. Plutonium(IV) on the other hand, is known to form strong complexes with most ligands, and undergoes strong hydrolysis reactions, even at pH 1. These hydrolyzed plutonium compounds are very insoluble. Therefore, the decreased solubility under reducing conditions may be interpreted in terms of chemical reduction of Pu(V) to Pu(IV), although the exact oxidation states have not been determined. Americium is always in the form of Am(III), and should show similar solubility over the Eh range studied here.

These preliminary observations begin to provide quantitative constraints on the hypothesis of Dr. Litaor that under periods of prolonged and heavy rain events, waterlogging of soil produces anoxic conditions, and that reduction of plutonium to a lower oxidation state could mobilize plutonium. The present

work indicates that strongly reducing conditions result in decreased mobility of plutonium.

The Influence of Microbes on Plutonium Redox State.

A proposal was made to "incubate" a soil sample for a month, and then determine if microbial action would reduce plutonium to a lower oxidation state. While this proposal has merit, it has not been well thought out. Due to the complications of working with microbes, and the relative failure of bioremediation applied to actinides in general, we feel that such an undertaking should only be carried out after consultation with a microbiologist familiar with actinide chemistry issues. A recommendation was made to first consult with Dr. A. J. Francis (Brookhaven), and Betty Strietelmeier or Dr. Jim Brainard (Los Alamos). If these microbiological experts feel that such an experiment has merit and are willing to help design such an experiment, it should be pursued. If these experts can not envision a simple and meaningful experiment, then we recommend that this endeavor not be pursued.

Filtration Studies.

By employing operational definitions of solubility as determined by filter-passing experiments, it was determined that that there is very little "dissolved" plutonium in solutions collected at gauging station GS03. Of particular importance is the observation that the majority of plutonium activity in solutions was found associated with particulate material, and that the concentrations of "dissolved" plutonium were only in the femto-molar range (10^{-15}M). Femto-molar concentrations of "dissolved" plutonium are similar to global fallout concentrations as measured around the world. The observation of very small quantities of "soluble" plutonium in this surface water at RFETS provides quantitative information that "dissolved" plutonium is only of minor importance as a migration pathway, and that efforts should be focused on particulate and colloid-facilitated transport in surface waters at RFETS. Preliminary analyses indicate that these particulates contain a high amount of organic carbon, consistent with the notion of colloidal material. The determination of such ultra-low concentrations should be accompanied by QA/QC documentation to demonstrate the ability to determine such low concentrations of actinides using radioactive counting techniques. This documentation can be developed between sampling campaigns.

Conceptual Model Development.

The initial conceptual model document is now complete and has been released. The Site is to be congratulated on completion of this important milestone. The conceptual model is needed to serve as a guide to direct future research, and to help focus efforts on the needs of the Site in general, and on surface water quality in particular.

Erosion Modeling.

The erosion modeling effort appears to be moving forward at a reasonable pace. It is clear that when all the bugs are worked out, and the different hillside models are coupled together, it will be a valuable tool with which to probe various erosion scenarios. Based on the observations of the ultra-filtration and redox studies in FY98, it appears "dissolved transport" may be quantitatively defined as a minor pathway in the conceptual model, shifting focus to primarily particulate transport pathways in FY99. The erosion model will be crucial for examining different particulate transport scenarios, and the possible effects of heavy rain events over many years. This model will also be important in coming up with an independent prediction of the amount of plutonium that migrates on the 903 hillside during a heavy storm event. This prediction should be compared with Dr. Litaor's results and estimate that 0.5Ci of plutonium moved across the 903 hillside during a heavy storm events during May 1995.

Uranium Geochemistry.

Jim Ball – Uranium geochemical modeling

The data available for evaluation of geochemical processes and transport (attenuation) modeling for the solar ponds plume was presented and discussed. Gaps in water quality data and in the sampling well distribution were described. The advisor's charge to the geochemical modeling investigators is to define tests based on the AMS thermochemical and transport network modeling conclusions. It is expected that this could include new sampling locations and needs for sample component analyses at new and existing sampling locations, as well as proposal of coupled, reactive transport modeling for components of the hydrologic and plume systems.

Craig Cowdery for Annette Primrose – results of uranium isotopic analyses on selected solar ponds plume and background samples

Results from an initial set of background and solar ponds plume samples, selected for ICP/MS analysis, were presented. The implementation of isotopic analyses is an excellent step forward in characterizing the site and quantitatively defining extent and remediation requirements for the solar ponds plume. This is how the integration of DOE remediation activities and research developments from Environmental Science Management Program (EMSP) are supposed to work. We would like to see plans for further characterization analyses and information on how these results are impacting remediation actions and plans.

RESRAD Modeling using K_d Values.

There are major concerns associated with the use of K_d values, measured by Honeyman and Santschi, in the RESRAD model. First, there are major uncertainties about these values, partially due to the use of data from simple extraction experiments. The solution phase concentration includes PuO_2^+ and $Pu(OH)_m^{4-m}$ dissolved species as well as $PuO_2 \bullet nH_2O$ colloidal and/or particulate species whose relative amounts and significance are unknown.

Similarly, the mechanism of association of Pu with the soil is unknown; e.g. is dissolved Pu chemisorbing via ion exchange and/or is colloidal Pu physically sorbing to the soil. Where Pu can be identified as being associated with particles, the composition of this phase needs to be cogently discussed – the oxide phase, PuO_2, is often used in the soils context without detailed characterization information. The simple oxide is both a significant oversimplification for Pu chemistry in aqueous systems and unlikely given the observed complex behavior of Pu in these soils. Multiple reservoirs of Pu in the soils are possible and likely, resulting in reactive inventories which are less than the total concentration in the soil during these desorption/dissolution experiments. Which sites of the soil are involved in these various sorption processes and what are the concentrations of the sorbing soil sites in units per square centimeters. Finally what is the active total surface area of the soil samples? All these parameters must be known in order to use the K_d values with confidence for different soil samples, or at a minimum to constrain site-specific K_d values.

Similar problems of unawareness about parameters to be used in any realistic modeling exist. For example, are the same species sorbing in the unsaturated, compact soil as in the shaken lab experiment of dispersed soil? Are the concentrations of sorbing sites per cm^2 the same in the compacted, unsaturated soil? Is (almost certainly not) the surface area per unit mass the same for the compacted soil as for dispersed soil? Of major concern is that the lab experiment reflects the K_d for a single theoretical plate in the transport path whereas in the bulk soil, it is probable that thousands of theoretical plates are associated with the actinide transport. This is actually a critical aspect of how RESRAD and other modeling codes implement the use of information from simplified experiments such as these. While this may be a conservative factor, a non-conservative aspect of the modeling, that must be evaluated, is the treatment of an unsaturated soil as if it were saturated. It is reasonable that all the compacted soil not in the saturated pathway would not be involved in the sorption process and cannot be included in the modeling calculations. This may lead to a significant underestimation of the migration rate.

Water Budget

During discussions on Keith Motyl's presentation on surface water conditions for closure, some of the components of a water budget were tabulated to explain water flow allotments from natural and anthropogenic sources. This tabulation however, was not given within the context of a water budget. We suggest that all discussions of water fluxes and reservoirs should be given within such a context. The water budget for the site is a fundamental part of the conceptual model that underlies surface water transport, groundwater transport, recharge, storage, and discharge. It should be consistently used as a framework of reference for those groups working on mass loadings, erosion, groundwater contamination, and surface water contamination. It would be helpful if the water budget could be summarized on a single page, and made available for comment and for reference. In addition,

estimates are needed for how closure will affect the water budget. For example, large caps, the loss of ponds, and the gain of wetlands will all affect the water budget and water flow paths. A second reference page outlining any significant changes in the water budget and flow paths that result from alternate remedial actions should also be provided. Finally, estimates should be made for the uncertainty associated with the components of the water budget. How much uncertainty is involved and how much uncertainty is acceptable?

Air Transport Modeling

Connection between erosion modeling and surface water particulate size analyses was discussed. These components of the AMS work are addressing parallel problems and complementary questions. Based on the short writeup provided prior to these meetings, the AMS Advisory Group requests that further information on the level of dose expected and/or possible for the contaminant resuspension and distribution be presented at an upcoming meeting. As results become available, the investigators should be encouraged to examine integration issues and conclusions.

Aseptic Groundwater Well Installation and Evaluation

The advisory team had a brief discussion about the rationale and approaches to validating the conceptual model conclusion that groundwater contamination by actinides observed in monitoring wells is the result of drilling and not transport through the system. The value of drilling aseptic wells, in which entrainment of contaminated surface soils is carefully avoided, was accepted. Priority sites are on the 903 Pad and in it's directly associated contaminated soil area.

Documents provided to advisory group

Loading analysis for the actinide migration studies at the Rocky Flats Environmental Technology Site, RF/RMRS-98-277.UN Rev 0, September 1998

Actinide content and aggregate size analyses for surface soil in the Walnut Creek and Woman Creek watersheds at the Rocky Flats Environmental Technology Site, RF/RMRS-98-281.UN, September 1998

Conceptual model for actinide migration studies at the Rocky Flats Environmental Technology Site, October 1998

Triay, I. R., and Loge, G. W., Batch experiments for desorption of plutonium and americium in contaminated soil from the Rocky Flats Plant, LA-UR-94-1165

Kung, K. S., Lu, N., Triay, I. R., Motyl, K. M., and Roushey, W. J., Chemical extraction of plutonium and americium for contaminated Rocky Flats soil. Radiochimica Acta 80, 13-21 (1998)

Santschi, P. H. Draft final report on phase speciation of Pu and Am for 'Actinide Migration Studies at the Rocky Flats Environmental Technology Site', 15 October 1998.

Keith Motyl, viewgraphs on Actinide Migration Study, Surface Water Endstate for RFETS Closure

Greg Wetherbee, viewgraphs on Endstate for RFETS Closure and AMS FY99 directions and final products

Air Modeling in Support of Actinide Migration Study (attached)

Evaluation of anthropogenic and naturally-occuring uranium in SPP groundwater (Draft 9/25/98)

Tour of Individual Hazardous Substance Sites in the Perimeter Area and Map

Documents requested for advisory group

Source Control Alternatives Analysis

Accelerating Cleanup: Path to Closure of RFETS, June 1998 *[dkn has copy and has provided it to other members of advisory group]*

Summary of existing data on actinides at RFETS (Annual RFCA Report?) *[Win will provide]*

Participants in AMS technical meetings

Ball, Jim	Honeyman, Bruce	Peters, Mike
Choppin, Greg	Janecky, David	Roberts, Rick
Chromec, Win	McCallister, Russell	Santschi, Peter
Clark, David	Motyl, Keith	Shelton, Dave
Corsi, John	Nordstrom, Kirk	Wetherbee, Greg
Cowdery, Craig	Paton, Ian	

AMS Participants in public meeting

Ball, Jim	Honeyman, Bruce	Shelton, Dave
Choppin, Greg	Janecky, David	Wetherbee, Greg
Chromec, Win	McCallister, Russell	
Clark, David	Nordstrom, Kirk	
Corsi, John	Santschi, Peter	

Participants in RFETS Protected Area Tour

Ball, Jim	Janecky, David	Wetherbee, Greg
Clark, David	Mewes, Jackie	
Corsi, John	Moore, LeRoy	
Gregory-Frost, Laurie	Nordstrom, Kirk	
Honeyman, Bruce	Santschi, Peter	

Air Modeling in Support of Actinide Migration Study
(provided by site to DRJ prior to meeting)

A confirmed significant pathway for off-site emissions from Rocky Flats (RFETS) is via the air. Monitoring data at the fenceline and downwind of significant fugitive source areas show ambient impacts that appear relatively well correlated with the sources of those emissions.

Resuspension factors have been empirically developed for RFETS that represent the gross relationship between surface soil contamination and air concentrations downwind of that contamination. However, the role of wind-blown resuspension has not been examined to understand the influence that larger airborne particles may have on the redistribution of contaminants in the environment. Fine airborne particles are readily carried many kilometers in the atmosphere and have been measured. Larger particles, on the other hand, may typically fall out within a few tens to several hundreds of meters. These larger particles will have the effect of replenishing surfaces previously eroded, and will contribute in some amount to the contaminant levels in a water channels and surface impoundments. The significance of these contributions is unknown.

The proposed air modeling is expected to contribute to our understanding of near-term effects on surface contaminant distributions during and immediately following an event with significant airborne emissions (such as an environmental restoration project). In addition, and in the longer view, the modeling will help to understand and map out the consequences of gradual airborne erosion on both soil contaminant distributions and changes in expected public dose for various fixed receptor locations.

In addition to the question of relative contribution to the water pathway, the following discussion suggests how air modeling may contribute to the actinide migration study. Simple dispersion modeling of windblown resuspended, contaminated soils has been performed. The results show that a small area of highly Pu-contaminated soils near the 903 Pad contributes about 30 percent of the dose received by a receptor at 96th and Indiana. Somewhat surprisingly, very low levels of Pu contamination from a somewhat larger area immediately adjacent to that same receptor can contribute a similar dose. Extending that observation, long-term redistribution (dilution, if you like) of the contamination from RFETS may not result in a significantly reduced dose to a typical receptor, but could actually lead to an increase in the average dose to more distant receptors, compared to present day estimates. This suggests the importance that air modeling could play in determining the focus and extent of cleanup efforts at the Site.

Work Scope Document for 'Actinide Migration Studies at the Rocky Flats Environmental Technology Site'
FY '99

Bruce D. Honeyman, Colorado School of Mines, and Peter H. Santschi,
Texas A&M University at Galveston

1. Overview.

The goal of the Actinide Migration Studies (AMS) is to provide data in support of Site closure, including: 1) soil action levels vis-à-vis surface water quality; 2) long-term disposition of the ponds; 3) 'far-field' actinide behavior during long-term closure.

A number of focus issues were identified during the August 17 and 18, 1998, meeting of the Actinide Migration Group (Advisory Team document of 8.19.98). Two broad areas of investigation emerged from group discussions for consideration for FY 1999 work by Honeyman and Santschi: 1) colloid characterization of surface waters and sediments (Santschi); 2) continuation of analysis of the potential for 'redox mobilization' of Pu and Am (Honeyman).

2. Justification.

A wide range of work at Rocky Flats has demonstrated that 'particulate' forms of Pu and Am make up a significant fraction of the actinide inventory in soils and suggests that surface water transport of Pu and Am is dominated by actinide associations with suspended solids. A clear understanding of the speciation of Pu is requisite for the development of defensible closure strategies. Generally speaking, laboratory analysis of ^{239,240}Pu indicates that, under 'normal' soil conditions, less than 0.5% of soil ^{239,240}Pu is 'soluble'. Furthermore, observations that, in some instances, ^{239,240}Pu/^{241}Am activity ratios in surface waters approach unity suggest that Pu and Am may not be 'locked' together in particulate form. Questions concerning the environmental form of Pu and Am have direct bearing on evaluating the importance of various migration pathways and in the development and refinement of Data Quality Objectives (DQO: i.e., model parameters and uncertainty levels).

3. Tasks.

3.1. Task 1: Continuation of analysis of the potential for 'redox mobilization' of Pu and Am (Honeyman).

3.1.1 Objective:

a. To determine if it is possible, under any set of environmentally relevant soil redox conditions, to 'solubilize' a significant fraction of RFETS soil Pu.
b. Elimination of reductive dissolution of soil host phases (under 'extreme' soil conditions) as a migration pathway or, if not eliminated, the condition necessary for such a pathway to be important.

3.1.2. Justification:

Data on the particle/solution partitioning of Pu and Am under a range of soil conditions are needed: 1) to develop and refine the conceptual model of actinide transport at RFETS; and 2) as input parameters for actinide transport models. A broad set of Site data is supportive of a model for Pu and Am fate at the Site which give primacy to low actinide solubility under 'normal' Site conditions and actinide mobility through particle transport. Data from FY '98 work suggests that

Pu 'solubility' under mildly reducing conditions my also be limited (i.e., less than 0.5% of the soil inventory). Furthermore, this analysis will allow us to generalize the results of the FY '98 work: to a range of solutions, including RFETS groundwater, as well as a range of soils and sediments.

3.1.3. Approach.

The primary question that will be answered during this contract period is this: Is it possible, under any set of conditions that would be representative of 'extreme' environmental conditions, to significantly solubilize RFETS Pu above the currently-observed levels of $\leq 0.2\%$ of the soil Pu inventory? If the solubiltity of Pu is not increased under 'extreme' conditions, relative to the solubility of Pu under 'normal' conditions, the Site can conclude that the dominant migration pathway for Pu, under all environmental conditions, will be through particle transport.

If it is possible to increase Pu solubility through some combination of E_H, system conditions (e.g., microbial growth) and time, the focus of the analysis will be to accurately delineate the set of conditions that would foster Pu solubilization.

Since each experimental approach is limited in its ability to simulate natural conditions, different approaches are needed. The electrolytic approach investigates how and when Pu in solution is reduced at the electrodes, while the microcosm approach evaluates the potential for remobilization from particles under microbially mediated reducing conditions likely encountered under water-logged conditions, potentially enhanced in electron donor species by animal wastes.

3.1.4. Analytical Plan:

The primary analytical direction will be an extension of experimental system for the electrochemical control of redox potential initiated in FY 1998. A second, exploratory (yes/no) experiment will be initiated to ascertain the utility of incubating soil isolates for the evaluation of redox control of Pu solubility. Analysis of Am will be made on all samples for which Pu is analyzed.

1. *Electrochemical control of redox potential and monitoring of Pu and Am concentrations as a function of decreasing redox potential.*

a). The electrochemical cell is effective at regulating the potential of dissolved or colloidal form of Pu. However, data from FY 98 show that the cell technique as currently employed does not apparently promote the reductive dissolution of Mn and Fe oxides. The first task of FY '99 will be to modify the technique to foster the reductive dissolution of soil-phase sesquioxides. One strategy that we will explore is to add charge-carrier ions to solution to aid electron transfer reactions away from the electrode (i.e., at particle surfaces). Duration: ca. 1.5 months.

b). Evaluation if there is indeed a plateau region for Pu concentrations in solution at intermediate redox potentials by carrying out analyses at redox potentials where one would expect *i*) Mn and *ii*) Fe to be reduced. Subsequent analyses will fill in points at lower redox potentials and will attempt to replicate the low Pu levels measured at low redox potentials (e.g., -100 mV). Duration: ca. 4 months.

c). Determination of the oxidation states of filter-passing Pu (e.g., Pu(IV), Pu(V)) to correlate with the E_H analysis, using methods developed by Choppin and others (e.g., Bertrand and Choppin, 1982; Saito and Choppin, 1983; Kobashi et al., 1988). Furthermore, we will want to evaluate the 'physical' speciation of Pu (i.e., whether Pu is present in truly dissolved or colloidal forms through the use of ultrafiltration and/or dialysis techniques). This suite of analyses will support RESRAD calculations and address the issues surrounding the relationship between

surface water quality and soil action levels (SAL). Duration: 1 month for ca. 4 samples; run concurrently with a and b. Colloidal analysis on an oxidized sample.
d). Evaluation of additional samples from the Site, as selected through discussions with the Advisory Group. Candidates include pond sediments and marsh sediments. Duration: ca. 1 month/E_H value.
e). In FY '99 we noticed that under reducing conditions the aggregation of suspended soil particles decreased. This observation suggests that reducing conditions may foster the release of colloidal Pu. This task includes the analysis of particle-size distribution under oxidizing and a reducing set of conditions.

2. *Simulation of prolonged water-logged conditions using a microcosm or incubation approach.*
f) Under certain conditions soil, microbiota are capable of fostering the rate and extent of redox transformations. For example, the annual 'turnover' of Pond C-2 and the coincidence between increased Mn and Pu concentrations in pond surface waters is suggestive of microbial effects on Pu solubility. This task will be exploratory, of about 2 weeks total effort and run in parallel with Task 1a.

The approach will be initiated in consultation with advice from a specialist in microbial effects on actinide biogeochemistry (e.g., A.J. Francis). The experimental system will consists of a sampling chamber (e.g., a Plexiglas tube 6" x 3") containing about several hundred grams of sediment or wetland material; the chamber will be sealed after sampling. The sample will be allowed to incubate in the chamber for several weeks before analysis. The redox potential can be calculated from measurements of oxygen, nitrate, Mn(II), Fe(II) concentrations, as well as other redox sensitive species. The oxidation states of Pu, and activity of Am, will be determined at the end of the incubation period. The decision to continue or desist will be made after consultation with the Actinide Advisory Panel.

3.1.5. Expected results (refer to timeline):
Results for the FY '99 will include:

- Establishment of Pu/Am solubility relationships over a range of E_H conditions relevant to RFETS and issues of surface water quality and soil action levels.
- Answer to a 'yes/no' question: Can deeply or prolonged reducing conditions lead to an increase in Pu and Am mobility?
- Completion of the E_H/actinide 'solubility' relationship through analysis of intermediate E_H values to confirm broad constancy;
- Analysis of Pu/Am 'solubility' under deeply reducing conditions (worst-case scenario);
- Analysis of particle aggregation/disaggregation under reducing conditions;
- Analysis of 'soluble' Pu oxidation state, to correlate with the E_H analysis;
- Thermodynamic modeling of Pu speciation as a function of E_H.
- To provide data needed to meet the DQO or the AMS.

3.1.6. Site support for sampling:
We anticipate the need for several soil or sediment grab samples from selected sites (in consultation with the Advisory Panel) to extend the redox analysis to a second (or third, if

possible) site. Task 1b will require a 'box core' for the incubation experiment. CSM personnel will observe all sample procurement.

3.1.7. Estimated Budget for all tasks: $150,000.

3.2. Task 2: Colloid characterization of surface waters and sediments (Santschi).

We propose for 1999 to continue the phase speciation work of Pu and Am in stream water, using different sites and smaller pore size filters than those used in 1998, as well as controlled laboratory experiments with resuspended stream sediments.

3.2.1. Objectives:

1. To determine the association of Pu and Am with: 1) particulate, 2) colloidal and 3) dissolved phases, and attempt to determine oxidation states of the dissolved phase, for field samples from a selected pond, pond release waters and compliance point baseflow waters, as well as for samples from controlled laboratory resuspension and repeated washing experiments from wetland samples.
2. Electrophoretic mobility measurements to determine the charge of colloids isolated from wetlands and surface waters.
3. To determine the chemical nature of the colloidal carrier phase (e.g., Fe, Mn, C, Al, etc.).
4. To provide data needed to meet the DQO of the watershed erosion modeling efforts.

3.3.2 Justification:

FY 98 work has demonstrated the likelihood that 'dissolved' Pu is predominantly in colloidal form. The issue of the speciation of 'dissolved' forms of Pu is crucial for understanding the relationship between surface water quality and soil action levels, as well as to support the scientific defensibility of RESRAD model simulations. The distribution of Pu and Am among different particles sizes and colloid molecular weights is important for developing management controls on surface water quality. The focus of this task is to determine the dominant oxidation state of the filter-passing Pu and Am species in stream water as well as those generated during sediment resuspension during controlled laboratory experiments, and to relate that information to composition and charge of colloids. Surface charge is an important colloid characteristic because it regulates the extent to which colloidal material interacts with particles and immobile soil media and, therefore, is a primary parameter for estimating the extent to which colloids are mobile and for the development of strategies for removing colloidal material and associated actinides from water through engineered systems.

3.2.3 Analytical Plan:

1) The first task of phase association of Pu and Am investigations consists of three sub-tasks: a) CFUF evaluation (e.g., model compound filtration efficiency) , b) surface water sampling, and c) colloid generation for marsh samples in controlled lab experiments. The sampling sites will be from a selected pond, pond release waters and compliance point baseflow waters. Exact sites to be sampled in the spring will be determined together with sites personnel. Grab samples will be collected by bailing water from the stream using a beaker followed by compositing the water into clean 15 to 20 L Nalgene carboys for processing and analysis at CSM. In addition, marsh samples will be collected for soil resuspension experiments with subsequent filtration and cross-flow ultrafiltration in the laboratory.

Since CFUF is not a standard analytical tool, system calibration will continue. About 20% of the task effort will be devoted to calibration issues. The protocols of Guo and Santschi (1996,1997) and Wen *et al.* (1996, 1998) will be followed for isolating colloidal and particulate phases of metals such Pu, Am from surface waters by CFUF will be followed. Chemical parameters to be measured include total organic carbon (TOC), dissolved organic carbon (DOC), colloidal organic carbon (COC), particulate organic carbon (POC), pH, alkalinity, Al, Fe and Mn of the water, and % organic carbon, Al, Fe and Mn in the colloidal and particulate phases, according to Guo and Santschi (1997) and Wen *et al.* (1998). These measurements will be conducted on the isolated aqueous solution phases or on resolubilized freeze dried material, or both.

Oxidation states of Pu solution species, if present at measurable concentrations, will be determined using methods described by Bertrand and Choppin, 1982; Saito and Choppin, 1983; Kobashi et al., 1988. Other pertinent papers on this subject are those of Choppin, 1991; Nitsche et al., 1988; and Saito et al., 1985.

2) Electrophoretic mobility experiments will be conducted using a 2-D polyacrylamide gel electrophoresis system, after radiolabelling of organic matter using ^{14}C (e.g., Wolfinbarger and Crosby, 1983; Quigley et al., 1998). The electrophoresis gels are sectioned at the end of each experiment, leached in 3ml of 1% SDS detergent for 24 hours, added to a scintillation cocktail and the final sample measured on a Liquid Scintillation Counter.

3) Aliquots of all samples will be kept for chemical determinations of carrier phases.

4) Data generated during this project will be interpreted in terms of the DQO of the watershed erosion modeling effort.

Strategy:
The strategy will be to start the resuspension and repeated washing experiments as soon as funding starts, which will allow us to characterize oxidation states and elemental compositions of carrier phases, and to initiate the electrophoresis experiments as soon as possible. Starting in spring, field samples will be taken in two sampling expeditions which can be conducted as close as two weeks apart, or as far as 3 months apart. During that phase, electrophoresis and composition work will also be carried out on colloids.

3.2.4. Expected results:
- Phase speciation (particulate, colloidal and dissolved) of Pu and Am in surface waters under different experimental and field conditions;
- Chemical speciation (i.e., oxidation state) of Pu in the dissolved form;
- Capacity of soils and marsh sediments to act as a source of colloidal carriers for Pu and Am;
- Elemental composition and charge of colloidal carrier phase.

3.2.5 Site support for sampling:
We anticipate the need for water samples from pond releases, compliance points, and grab samples from marsh sites.

3.2.6. Estimated Budget: $100,000

3.3. Task 3: Meetings.
Three two-day meetings at RFETS with two days prior to the meetings set aside for the review of meeting-related documents.

4. Quality Assurance/Quality Control.
Rocky Flats Environmental Technology Site Analytical Services Division Modules RC01-B.2 (Isotopic determinations by alpha spectroscopy) and GR01-B.1 (General laboratory requirements) will provide guidance, where appropriate, for QA/QC protocols. Documentation of FY 97 work will follow procedures to be established through discussions between CSM, TAM and Site QA/QC personnel. The Data Quality Objectives outlined in the Actinide Migration Study Data Quality Objectives final document will serve as the framework of recording and reporting the results of these investigations (i.e., PARCC requirements).

Limits on data uncertainty will correspond to the required margin of uncertainty specified for final computed parameters, as outlined in the data quality objectives (DQO). With respect to the outlined task, there are three major sources of error contributing to overall parameter uncertainty: 1) accuracy with respect to instrument calibration; 2) random analytical error; 3) sample representativeness. Errors 1 and 2 will be minimized through standard laboratory protocols for instrument calibration and replicate sample analysis. Fundamental to the successful completion of this task is development of a strategy to determine the sample size (error 3) that will permit the baseline reproducibility required to meet the specified margins of uncertainty (e.g., $\pm$ 10% uncertainty in phase distribution). The margin of uncertainty on computed parameters will correspond to those specified on the final AMS DQO document.

The use of plutonium and americium at the Colorado School of Mines and Texas A&M University is regulated by the states of Colorado and Texas, respectively. Training of personnel is governed by each of the university's radioactive materials licenses. Worker Health and Safety at CSM and TAM is governed by the respective university health and safety department.

1. Schedule and deliverables.

Task	Time requirement	Target completion
1. 'Redox' mobility.	10 months	31 July 1999
2. Colloid and particulate associations of Pu and Am.	2 months preparation, 2 months for sampling, 3 months for laboratory experiments, 3 months for sample processing	31 July 1999
3. QA/QC	2 months throughout the project	31 July 1999

Reports:
Monthly updates on projects tasks in 'bullet form'.
Interim Project Report due at Kaiser-Hill for internal review: 15 August 1999
Receipt of comments on Draft Final Report: 1 September 1999
Final Project Report due at Kaiser-Hill: 30 September 1999

The Final Project Report will contain the following sections:

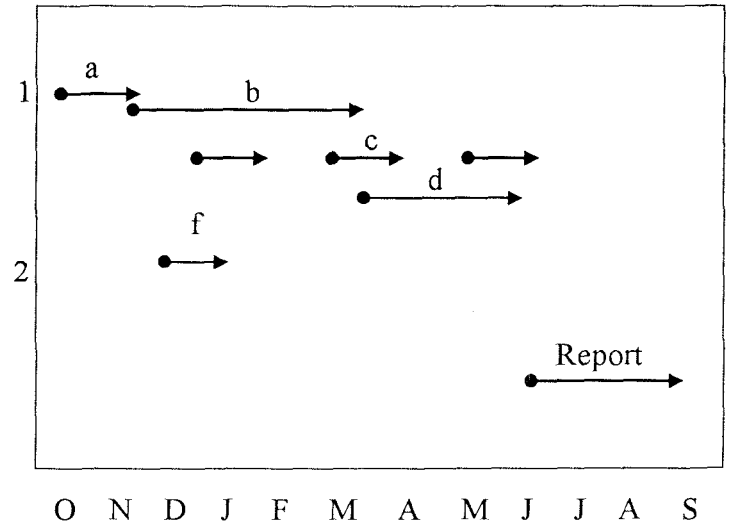
- **Methods and Procedures**.
  Complete descriptions of methods used such that the work could be reproduced by personnel of similar qualifications and resources.

- **Results and Discussion**.
  This section will present and describe the results of the FY 1998 work. The results will be related to findings of previous investigations. The results will also be discussed in terms of their applicability to the data needs of the conceptual model.

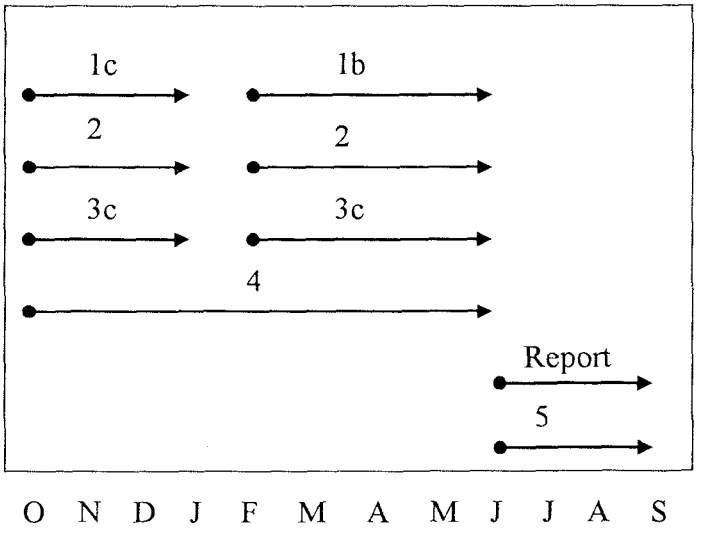
- **QA/QC**.
  Analytical data for both target environmental samples and QA/QC samples with uncertainties, MDA's, and a clear description of the methods for calculating the MDAs and uncertainties; an analysis of data quality as pertains to Data Quality Objectives.

Schedule of tasks. The letter designations refer to the sub-tasks.

Redox Tasks



Colloid Tasks



6. References.

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Actinide Migration at the Rocky Flats Environmental Technology Site

Air Pathway Fiscal Year 1999 Work Plan

1.0 Background

The Rocky Flats Environmental Technology Site (Site) has been a source of airborne actinides throughout its history. Over time, small amounts of plutonium and other actinides have been deposited on or mixed with surface soils at the Site. Wind or mechanical disturbance of the contaminated soil can result in actinide-laden soil particles becoming airborne (i.e., being resuspended). The actinide-containing particles will be transported some distance downwind before being redeposited on the ground or in water by a variety of mechanisms that remove particles from the air, such as rainout or dry deposition. As a result, airborne migration is one of several transport pathways (others include soil erosion, surface and groundwater movement, etc.) that redistribute actinides in the environment in the vicinity of the Site.

The major source areas that contribute to airborne actinides at the Site are the 903 Pad and the adjacent "lip" area. The 903 Pad was contaminated with plutonium- and americium-laden cutting oil stored in metal drums, which over time leaked onto the soil beneath the drums. Removal of the drums in the late 1960's and associated cleanup activities resulted in dispersion of contaminated soil to the east and to the south of the 903 Pad. The storage area was covered with asphalt in 1969, and is no longer a source of resuspendable actinides. However, the initial spread of plutonium- and americium-contaminated soil prior to the installation of the asphalt pad has resulted in a plume of actinides in the surface soils extending to the east and southeast from the 903 Pad itself.

Between 1989 and 1995, resuspension of actinide-contaminated soils and transport through the air pathway occurred primarily due to natural processes, such as rain splash or wind erosion. Remediation of contaminated soils and waste-disposal areas at the Site began in 1995. Such activities disturb contaminated soils and result in additional airborne particulates. Future resuspension of actinide-containing material will occur due to both natural and anthropogenic activities.

2.0 Fiscal Year 1999 Air Pathway Task Summary

The Actinide Migration Studies Group, convened by the Department of Energy (DOE) in 1996, recommended that a conceptual model for actinide transport be developed to establish relationships between the Site's physical and chemical characteristics and the fate and transport of radionuclide contaminants in the environment. Fiscal year 1999 (FY99) activities associated with this effort

must be processed into sequential, hourly data and formatted for use in the selected model.

6. Implement model to predict ambient air concentrations and deposition of actinides to soil and water on or around the Site. The deposition estimates will be used as input to the models for other transport pathways (e.g., soil erosion, surface and groundwater transport), and will be used along with air concentration projections to form the basis for air pathway dose estimates.

7. Investigate previous risk assessment studies that calculate radionuclide dose based on ambient mass concentrations and deposition. Evaluate and select a method to convert air concentrations and deposition estimates to radioactive dose; calculate air pathway dose at specified locations on or around the Site.

8. Perform sensitivity analyses of emission rates and deposition parameters and their effects on projected dose. If feasible, verify model estimates using data from existing monitoring programs at the Site. The purpose of this task is to provide information about where future efforts should be concentrated to improve model performance and the accuracy of resulting dose estimates.

9. Prepare interim and final summary reports of FY99 results including actinide deposition rates, dose estimates for various resuspension mechanisms, refined resuspension factors, and sensitivity analysis results; and recommend approach to quantify long-term migration of airborne actinides in future studies. Also recommend future air pathway work, such as integrating results with watershed erosion studies, examining various "what if" scenarios, and expanding the capability of the modeling tool, as appropriate.

The discussion below expands on the key tasks identified above.

3.0 Emission Rates

Emission rates (source term) are critical input parameters for a Gaussian plume dispersion model because they are directly proportional to the resulting ambient air concentration and deposition rate projections produced by the model. Previous studies at the Site have shown that emissions of particulates and associated actinides from remediation activities are orders of magnitude greater than those due to natural processes alone. The major focus of this task will be to quantify actinide emissions from planned remediation activities, although natural resuspension processes will also be considered.

In the absence of remediation or other anthropogenic activities that disturb contaminated soil or debris, natural processes have been the dominant resuspension mechanisms at the Site. Previous studies of actinide resuspension at the Site have examined four natural processes: saltation (wind erosion of bare soil), rain splash (which moves soil particles from the ground onto vegetation

Radian's proposed compromise will be to use a relatively sophisticated dispersion and deposition model to estimate actinide migration for each isotope of interest, then use a separate algorithm to convert actinide concentrations to dose units (see Section 5.0 regarding dose assessment). Radian will use the most recent version of the ISC3 Short-Term Model (ISCST3 Version 98226) to perform refined dispersion and deposition modeling. ISC3 was developed and is supported by EPA to handle multiple source types (stacks, fugitive areas) and predict concentrations and/or dry/wet deposition. The latest improvements in dry deposition modeling have been implemented in the model.

Three critical input data sets will be assessed in this task: emission rates, which are described above, meteorological data, and particle size distribution data to calculate deposition. The latter two required data sets are described below.

Surface meteorological data are available from on-Site monitors. Upper air data will be obtained from Denver International Airport. Surface and upper air meteorological data in "raw" form must first be processed before use in the dispersion model. The data requirements include wind direction, wind speed, dry bulb temperature, opaque cloud cover, cloud ceiling height, and twice daily mixing heights.

ISC requires the following particle-size specific parameters as input: particle diameter categories, mass fractions, and particle densities. A key task will be to evaluate particle size distributions for resuspended material at the Site and to determine actinide activities for each particle size category.

5.0 Dose Estimation

As mentioned earlier, the weakness of the ISC3 model for the task at hand is that it does not estimate radioactive dose. In contrast, dose models like CAP88-PC have "built in" dose conversion factors. There are two primary options to obtain dose estimates from the ISC3 calculations: 1) extract dose conversion factors from a dose model like CAP88-PC and post-process ISC3 results; or 2) import ISC3 calculated concentration and deposition values into CAP88-PC or a similar model to obtain cumulative dose. This task will evaluate, select, and implement the most cost-effective option.

6.0 Sensitivity Analyses

A sensitivity analysis will be performed to examine the effects of emission rates from each natural and anthropogenic resuspension mechanism on the predicted dose. The objective of the analysis will be to determine which mechanisms have the largest contribution to total predicted dose and to investigate how variability in source term characterization may affect dose estimation.

WORK PLAN

GEOCHEMICAL SUPPORT FOR THE ACTINIDE MIGRATION STUDIES AT THE ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE

December 10, 1998

Rocky Flats Environmental Technology Site
Golden, Colorado 80402

USGS
science for a changing world

CONTENTS

INTRODUCTION

Purpose

The purpose of this work plan is to provide a framework for geochemical support for uranium transport modeling for the Actinide Migration Studies (AMS) at the Rocky Flats Environmental Technology Site (Site). The AMS was implemented to investigate the mobility of plutonium, americium, and uranium in the Site environment. The goal of the AMS is to answer the following questions in the order of urgency shown.

1. Urgent: What are the important actinide migration sources and migration processes that account for recent surface water quality standard exceedances?
2. Near-Term: What will be the impacts of actinide migration on planned remedial actions? To what level do sources need to be cleaned up to protect surface water from exceeding action levels for actinides?
3. Long Term Onsite: How will actinide migration affect surface water quality after Site closure? In other words, will soil Action Levels be sufficiently protective of surface water over the long term?
4. Long Term Offsite: What is the long term off-site actinide migration, and how will it impact downstream areas (e.g. accumulation)?

Geochemical modeling and the analysis of groundwater interactions between water and geologic materials is important to understanding the solubility and mobility of uranium, which is very soluble and easily transported in groundwater. In addition, geochemical modeling provides an independent constraint on the range of uranium solubility for comparison with empirical information on soil-water uranium partitioning and for incorporation into groundwater transport models for actinide. Recent studies have produced results confirming that Pu and Am are neither present nor transported in groundwater in measurable concentrations. Additional studies indicate that essentially all Pu and Am previously thought to have infiltrated into the groundwater were transported to the subsurface by the well drilling process. Consequently, Pu and Am are not the focus of this study.

Several areas of the Site, including the Original Landfill and Ash Pits, the Solar Ponds Area, and other potential Industrial Area sources, contain uranium contamination. The Solar Ponds area contains uranium and nitrate groundwater plumes; portions of the uranium plume have been difficult to distinguish from natural background uranium. The migration of these plumes has been impacted by the Interceptor Trench System that collects most, but not all, alluvial groundwater. The nitrate groundwater plume has impacted the North Walnut Creek watershed. In selecting and designing a remedial system, the geochemistry of the uranium and its interaction with major cations and anions, including nitrate, needs to be evaluated.

Scope

For fiscal year 1999 (FY99), the USGS support to the AMS will include the following:

- Review, evaluate, and summarize groundwater geochemistry data and interpretations at the Site to provide the context for geochemical modeling.
- Review uranium thermodynamic data and uncertainties for the geochemical calculations, for the purpose of error propagation;
- Perform geochemical modeling calculations to evaluate groundwater data quality and usefulness for determining solubility constraints on uranium concentrations at the site;
- Assist Project Teams in evaluating uranium geochemistry and transport.

The USGS will collaborate with the remedial action project teams in an advisory/oversight capacity to evaluate the following: (1) natural vs. man-made uranium contamination; (2) uranium geochemistry aspects of potential remedial alternatives; (3) potential interactions between uranium and other contaminants; and (4) effectiveness of removal strategies. This knowledge will be useful for potential future remediation of the Solar Ponds Plume, the 903 Pad/Lip Area, Original Landfill, and the Ash Pits.

The USGS will conduct an analysis of uranium geochemistry that will include evaluating how thermodynamic data will be used to describe uranium speciation, solubility, and potential interactions with nitrate and other solutes. The results of the analysis will be summarized in a report that will be reviewed by the AMS Group.

Uranium sorption cannot be modeled; however, results of examination of whether uranium solubility constraints are adequate to explain dissolved uranium concentrations have the potential to suggest whether or not adsorption could play a significant role. Laboratory studies would be needed to adequately characterize uranium sorption and the USGS is not equipped to perform such studies.

Data Sources and Description

Data for this analysis will come from the following Site monitoring programs:

- Event-Related Surface Water Monitoring Program, 1991-1994;
- Industrial Area IM/IRA Monitoring Program, 1995-Present;
- Rocky Flats Cleanup Agreement (RFCA) Monitoring Program: 1996-Present; and
- Source Evaluation and Preliminary Mitigation Program: 1997-Present.
- Integrated Monitoring Plan, RFETS, Draft, May, 1998

Geochemical Codes and Data Bases

Two geochemical modeling computer programs will be used; WATEQ4F and PHREEQC. These are described below.

- WATEQ4F: This speciation/solubility code is well suited for evaluating data completeness and accuracy, and for simpler geochemical questions such as saturation indices for solids of interest. WATEQ4F includes calculations for uranium. The uranium data base is based on the publication of Grenthe et al. (1992), which represented a significant advance in the scientific community's knowledge of uranium thermodynamic data. The thermodynamic data base is one source of uncertainty in the geochemical calculations. As such, it is necessary to define the range of these uncertainties and their effect on the geochemical modeling results. Important U aqueous complexes include $U(OH)_4^0$, $UO_2(CO3)_2^{2-}$, and $UO_2(CO3)_3^{4-}$. Important U equilibrium solid phases include UO_2, $UO_2(OH)_2$, and U_3O_8.

- PHREEQC: This speciation/solubility/adsorption/solute-transport code is the newest and most powerful USGS code of its type, and uses the complete WATEQ4F data base.

Study Area

The study area is limited to the Site from the west fence line to the east line, including the Industrial Area, Original Landfill, Ash Pits, Woman Creek, Walnut Creek, and South Interceptor Ditch (SID). The study area is limited to the Site property from the west fence line to the east fence. Data are limited or do not exist for thorough computation of uranium loading, but projections will be made based on existing monitoring results.

Data Compilation

The data used for this study will come from Site groundwater monitoring wells and will include the parameters listed in Table 1. The required resolution for the data are also shown in Table 1.

Table 1.—Data needs for uranium loading analysis in support of AMS modeling activities.

Parameter	Required Resolution for Analysis
Major cations (Ca, Mg, Na, K)	0.1 mg/L
Major anions (Cl, SO_4, NO_3, HCO_3)	0.1 mg/L, 0.1 mg/L, 0.1 mg/L, 1 mg/L
Uranium-234 (U-234)	0.02 pCi/L
Uranium-238 (U-238)	0.02 pCi/L
Uranium-236 (U-236)	0.02 pCi/L

These data will be compiled for computation of the uranium loads.

Data Analysis and Interpretation

The following review and computational tasks will be performed:

- Utilize uncertainties for U thermodynamic data to determine its reliability and applicability.
- Work with Site personnel to screen, evaluate, and select available groundwater chemistry data, especially with respect to uranium, nitrate, iron, manganese and dissolved oxygen.
- Work with Site personnel to evaluate and identify QA/QC protocols that have been applied to the data. Such protocols include spike recoveries, replicate analysis, alternative methods, and standard reference materials.
- Work with Site personnel to clearly identify uncertainties and standard error estimates in the data set to facilitate sensitivity analysis calculations.
- Screen data by examining charge imbalance (CI, should be less than 10 percent) and measured versus calculated conductance. Simple graphical techniques will be applied to help identify sources of analytical error.
- Use ion plots to formulate hypotheses concerning geochemical processes. Plots of cations with respect to the most conservative anion or anions are particularly helpful.
- Correlate (and/or plot) major and minor element chemistry of Site groundwater at selected locations to outline the attenuation of dissolved uranium and how it may be affected by redox, nitrate, dissolved organics, pH, and dissolved CO_2 species.
- Determine solubility controls on U by examining saturation indices (SI values) calculated using WATEQ4F.

Sensitivity Analysis

Use sensitivity analysis testing to determine the sources of variability of dissolved U concentrations over expected ranges of pH and Eh using the WATEQ4F thermodynamic data base and available chemical analyses of groundwater.

Schedule

The uranium geochemical support activities will begin on December 15, 1998 and finish no later than September 30, 1999 in support of the schedule for AMS modeling of soil erosion and surface-water transport processes. Compilation of uranium thermodynamic data will begin 12/15/98, with screening and evaluation of water analysis data to be completed by 1/29/99. Ion plots are projected for completion by 3/12/99, and geochemical modeling calculations will be done and screened and evaluated by 5/7/98. Sensitivity analysis calculations and their interpretation and evaluation will be done by 7/9/99, and a descriptive, interpretive report containing recommendations will be drafted by 8/31/99, with a final report completed by 9/30/99.

The above schedule is presented in tabular form in Figure 2.

Deliverables

Results of the analysis will be published in a succinct interpretive report. The report will contain tables and graphs displaying the following information:

- Overview of dissolved uranium and associated chemical parameters in groundwater at the Site;
- General origin and evolution of groundwater chemistry with special emphasis on factors affecting uranium migration;
- Outline of geochemical constraints on uranium mobility based on geochemical model calculations;
- Estimates of uncertainties in the modeling results and their meaning. Uncertainties will be determined in part by uncertainties in the analytical data; and
- Estimates of the maximum quantities of uranium (per unit area) that might remain in Site soils and result in maintenance of acceptable surface-water quality.

Figure 2.—Schedule for the Geochemical Modeling Tasks.

Task	Time Requirement	Target Completion	Resource Names
1. Data compilation	36h	1/29	Ball
2. Screening & Evaluation	24h	2/28	Ball
3. Ion plots	50h	4/15	Ball, Nordstrom
4. modeling, correlation	80h	5/30	Ball, Nordstrom
5. Sensitivity Analysis	70h	7/31	Ball, Nordstrom
6. Draft report preparation	60h	8/31	Ball, Nordstrom
7. Review comments due		9/15	Group Members
8. Final Report preparation	20h	9/30	Ball, Nordstrom

Schedule of Tasks.